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THE THEORY OF COMPLEX SPECTRA II*

By E. U. Condon and G. H. Shortley
Palmer Physical Laboratory, Princeton University

(Received March 20, 1931)

Abstract

Formulas for the relations between the energies of multiplets arising from the same electron configuration for all two-electron configurations up to *ff* and several cases of three-electron configurations are worked out following Slater's method; Slater's table of *a*'s and *b*'s being extended to cover *f* electrons. A systematic comparison of the known data with this first order perturbation theory shows poor agreement in many cases and good agreement in many. The theory predicts the observed alternation in the relative positions of singlet and triplet through *S*, *P*, *D*, *F*, etc. in the *pp*, *pd*, and *pf* triads, and the *dd* and *df* pentads. In general the *p* electron configurations fit very poorly; a uniform trend with atomic number is observed for p^3 and good fits are obtained for $4p3d$ in Ti III, V IV, and Cr V. For *d* electrons the theory fits very well in the first long period of the periodic table, and fairly well in the second. The ^1S of d^2 and the ^2D of d^3s are predicted much higher than the levels assigned to those multiplets when such an assignment is made. d^3 fits well except for ^2P. An energy level table of La II is given as recently analysed by Meggers and Russell. Here we have complete $5d4f$ and $4f^2$ configurations which fit the theory very well, these calculations having assisted in the assignment of some of the singlets and resulted in a rearrangement of singlet lines.

§1. Introduction

THIS paper is a sequel to one[1] published last fall in which the first steps were taken toward working out the second approximation for atomic spectra with Russell-Saunders coupling. Before going on with that work it was thought desirable to make a careful study of the application of the first approximation formulas, given by Slater's method,[2] to all of the known data. That is the subject of this paper.

It will be recalled that the first-order calculation gives formulas for the energy of each of the multiplets arising from a given electron configuration in terms of certain integrals taken over the radial factor of the wave function for an electron in the central force field that lies at the basis of the calculations. These integrals represent the perturbation energy due to the electro-

* This paper was presented at the New York Meeting of the American Physical Society, February 27, 1931.

[1] Condon, Phys. Rev. **36**, 1121 (1930).

[2] Slater, Phys. Rev. **34**, 1293 (1929).

static repulsion of the electrons. It is inconvenient to work out these integrals for they involve the unknown wave functions of the screened average force field in which the electrons move. Instead these integrals are treated as adjustable (except for restrictions such as that certain of them are essentially positive, etc.) in order to see how well the data can be represented. If a good fit is obtained that is, therefore, only a partial confirmation of the theory, for the question still remains open whether the relative magnitudes assumed for the several integrals are really compatible with their definition as integrals.

Since Meggers and Russell[3] have recently obtained for the first time, in La II, complete sets of multiplets involving the two-electron configurations pf, df, f^2 we have thought it worthwhile to extend Slater's tables of a's and b's to provide the necessary coefficients for applying the method to configurations involving f electrons. These results are presented in §2. In §3 and §4 the explicit formulas are given for the first-order energies in a number of important configurations and in §5, §6, and §7 comparison of the formulas with the data is made.

§2. Slater's Coefficients for f Electron Configurations

In Slater's paper[2] there are a few details connected with normalization that need to be straightened out. Slater, in his manuscript, had normalized his wave functions in an unusual way: namely, so that the normalizing integral over the spherical harmonic factor was set equal to 4π instead of 1. This requires the normalizing integral over the radial coordinate to be set equal to $1/4\pi$. When his paper went through the Physical Review office one of us (E.U.C.) thought that a mistake had been made in the normalizing factor and inserted a $(2\pi)^{-\frac{1}{2}}$ to normalize the $\Phi(m_l/\phi)$ on page 1308 in the usual way. As Slater was in Europe at the time he did not have an opportunity to set the matter straight again. Therefore this factor should be removed from the $\Phi(m_l/\phi)$ on page 1308 and then it should be borne in mind, what Slater does not mention, that the radial wave-function is to be normalized to $1/4\pi$ instead of 1. The usual normalization of each factor to 1, is the one we prefer. To have this one needs to leave the Φ factor as printed on page 1308, to insert $2^{-\frac{1}{2}}$ on the right side of the equation defining $\Theta(lm_l/\theta)$ on that page, to remove the factor 4π in the equation for $I(nl)$ on page 1310 and the factor $(4\pi)^2$ in the equations for $F^k(nl; n'l')$ and $G^k(nl; n'l')$ on page 1311.

We have also found it convenient to treat the a's and b's of page 1311 as integers by associating the denominator of the a's and b's as they occur in the tables of page 1312 with the corresponding F. Therefore we write

$$F_k(nl; n'l') = \frac{1}{D_k} F^k(nl; n'l')$$

where F^k is Slater's F and D_k is the denominator of the fractional value for $a^k(l, m_l; l'm_l')$ as given on page 1312. The corresponding definition of G_k is also made.

[3] See §7 of this paper.

Having detected an error in Slater's table of b's by reaching an inconsistency in deriving the energy levels for the *pd* configuration it was thought worthwhile to check these tables by a complete recalculation using Gaunt's formulas[4] for the integrals. These formulas were also used to extend the tables to the pairs, *sf*, *pf*, *df*, *ff*. This straightforward but laborious computation makes us now feel confident that there are no errors in Slater's table of page 1312 except the one originally detected. The value

$$b^3(1, \pm 1; 2, \mp 2) = 45/245$$

is correct, instead of 9/245 as printed.

The extension to f electron values is covered in Tables I and II.

TABLE I. *Extension of table of* $a^k(lm_l; l'm_l')$

Electrons	l	m_l	l'	m_l'	$k=0$	2	4	6
sf	0	0	0	±3	1			
				±2	1			
				±1	1			
				0	1			
pf	1	±1	3	±3	1	5/75		
	1	±1	3	±2	1	0		
	1	±1	3	±1	1	− 3		
	1	±1	3	0	1	− 4		
	1	0	3	±3	1	−10		
	1	0	3	±2	1	0		
	1	0	3	±1	1	6		
	1	0	3	0	1	8		
d^2	2	±2	3	±3	1	10/105	3/693	
	2	±2	3	±2	1	0	− 7	
	2	±2	3	±1	1	− 6	1	
	2	±2	3	0	1	− 8	6	
	2	±1	3	±3	1	− 5	−12	
	2	±1	3	±2	1	0	28	
	2	±1	3	±1	1	3	− 4	
	2	±1	3	0	1	4	−24	
	2	0	3	±3	1	−10	18	
	2	0	3	±2	1	0	−42	
	2	0	3	±1	1	6	6	
	2	0	3	0	1	8	36	
ff	3	±3	3	±3	1	25/225	9/1089	1/7361.64
	3	±3	3	±2	1	0	−21	− 6
	3	±3	3	±1	1	−15	3	15
	3	±3	3	0	1	−20	18	− 20
	3	±2	3	±2	1	0	49	36
	3	±2	3	±1	1	0	− 7	− 90
	3	±2	3	0	1	0	−42	120
	3	±1	3	±1	1	9	1	225
	3	±1	3	0	1	12	6	−300
	3	0	3	0	1	16	36	400

Note: In cases with two ± signs, the two can be combined in any of the four possible ways.

§3. THE ENERGY LEVELS IN TWO-ELECTRON CONFIGURATIONS

Slater has treated in detail the method whereby the energy levels of the several multiplets are to be found in terms of the F and G perturbation integrals and has given some examples. He has shown that the electrons in

[4] Gaunt, Phil. Trans. Roy. Soc. **A228,** 151 (1929).

closed shells are without direct effect on the perturbation theory, although of course, they have the indirect effect of determining the nature of the best

TABLE II. *Extension of table of* $b^k(lm\,;\,l'm_l')$

Electrons	l	m_l	l'	m_l'	$k=0$	1	2	3	4	5	6
sf	0	0	3	±3				1/7			
	0	0	3	±2				1			
	0	0	3	±1				1			
	0	0	3	0				1			
pf	1	±1	3	±3			45/175		1/189		
	1	±1	3	±2			30		3		
	1	±1	3	±1			18		6		
	1	±1	3	0			9		10		
	1	0	3	±3			0		7		
	1	0	3	±2			15		12		
	1	0	3	±1			24		15		
	1	0	3	0			27		16		
	1	±1	3	∓3			0		28		
	1	±1	3	∓2			0		21		
	1	±1	3	∓1			3		15		
df	2	±2	3	±3		15/35		10/315		1/1524.6	
	2	±2	3	±2		5		20		5	
	2	±2	3	±1		1		24		15	
	2	±2	3	0		0		20		35	
	2	±1	3	±3		0		25		7	
	2	±1	3	±2		10		15		24	
	2	±1	3	±1		8		2		50	
	2	±1	3	0		3		2		80	
	2	0	3	±3		0		25		28	
	2	0	3	±2		0		0		63	
	2	0	3	±1		6		9		90	
	2	0	3	0		9		16		100	
	2	±2	3	∓3		0		0		210	
	2	±2	3	∓2		0		0		126	
	2	±2	3	∓1		0		10		70	
	2	±1	3	∓3		0		0		84	
	2	±1	3	∓2		0		25		112	
	2	±1	3	∓1		0		15		105	
ff	3	±3	3	±3	1		25/225		9/1089		1/7361.64
	3	±3	3	±2	0		25		30		7
	3	±3	3	±1	0		10		54		28
	3	±3	3	0	0		0		63		84
	3	±2	3	±2	1		0		49		36
	3	±2	3	±1	0		15		32		105
	3	±2	3	0	0		20		3		224
	3	±1	3	±1	1		9		1		225
	3	±1	3	0	0		2		15		350
	3	0	3	0	1		16		36		400
	3	±3	3	∓3	0		0		0		924
	3	±3	3	∓2	0		0		0		462
	3	±3	3	∓1	0		0		42		210
	3	±2	3	∓2	0		0		70		504
	3	±2	3	∓1	0		0		14		378
	3	±1	3	∓1	0		24		40		420

Note: In cases where there are two ± signs, the two upper or the two lower signs must be taken together.

central field on which to base the approximation. Therefore, we do not need to give the details of the calculations but merely summarize the results.

Slater's F^k integrals are necessarily positive and decreasing with increas-

ing k, from their definition. Therefore, since the denominator D in the definition of our F_k increases rapidly, F_k necessarily decreases very rapidly with increasing k. Since the G's are not essentially positive by definition, no definite statement can be made concerning their relative magnitudes; however, in every instance we have found, the G_k's have been positive and rapidly decreasing with k. Although not consistent with its definition as an integral, it is convenient to measure F_0, which occurs in the formula for each multiplet, from an arbitrary low level of the spectrum. (Slater's theory provides an integral I, dependent only on the configuration, to locate the height of the whole multiplet.)

If one electron is in an s state the result is simply a singlet and triplet whose L is the l of the other electron outside closed shells, as Slater shows on page 1315, duplicating by this method a result of Heisenberg.

For pp, non-equivalent p electrons, Slater gives the triplet intervals. The complete formulas are, if ^3P is written for "relative energy of the center of gravity of the ^3P terms,"

$$\begin{aligned}
^1S &= F_0 + 10F_2 + G_0 + 10G_2 \\
^3S &= F_0 + 10F_2 - G_0 - 10G_2 \\
^1P &= F_0 - 5F_2 - G_0 + 5G_2 \\
^3P &= F_0 - 5F_2 + G_0 - 5G_2 \\
^1D &= F_0 + F_2 + G_0 + G_2 \\
^3D &= F_0 + F_2 - G_0 - G_2
\end{aligned} \qquad (pp)$$

We note that the arithmetic mean of the corresponding singlet and triplet energies is independent of the G's while corresponding singlet-triplet intervals are independent of F's. Also since $G_2 \ll G_0$ usually we have $^1S > {}^3S$ and $^1P < {}^3P$ and $^1D > {}^3D$; an alternation which is quite a general prediction of the theory.

For p^2, equivalent p electrons, the ^3S, ^1P and ^3D are ruled out by the exclusion principle and the formulas for what is left are the same as those for the arithmetic means of singlet and triplet in pp, namely

$$\begin{aligned}
^1S &= F_0 + 10F_2 \\
^3P &= F_0 - 5F_2 \\
^1D &= F_0 + F_2.
\end{aligned} \qquad (p^2)$$

The formulas for dd and d^2, also ff and f^2, show similar relationships. For dd we have

$$\begin{aligned}
^1S, {}^3S &= F_0 + 14F_2 + 126F_4 \pm (G_0 + 14G_2 + 126G_4) \\
^1P, {}^3P &= F_0 + 7F_2 - 84F_4 \mp (G_0 + 7G_2 - 84G_4) \\
^1D, {}^3D &= F_0 - 3F_2 + 36F_4 \pm (G_0 - 3G_2 + 36G_4) \\
^1F, {}^3F &= F_0 - 8F_2 - 9F_4 \mp (G_0 - 8G_2 - 9G_4) \\
^1G, {}^3G &= F_0 + 4F_2 + F_4 \pm (G_0 + 4G_2 + G_4)
\end{aligned} \qquad (dd)$$

where the upper sign is for the singlet and the lower for the triplet. For d^2 the multiplets are ^1S, ^3P, ^1D, ^3F, ^1G and their energies are given by the same formulas upon omitting the terms involving G integrals.

For pd the formulas are

$$\begin{aligned} {}^1P, {}^3P &= F_0 + 7F_2 \pm (\ G_1 + 63G_3) \\ {}^1D, {}^3D &= F_0 - 7F_2 \mp (3G_1 - 21G_3) \\ {}^1F, {}^3F &= F_0 + 2F_2 \pm (6G_1 + 3\ G_3). \end{aligned} \qquad (pd)$$

This shows the same alternation in sign of the leading G integral but differs from the preceding ones in that the F and G parts are not similar.

The formulas for pf are

$$\begin{aligned} {}^1D, {}^3D &= F_0 + 12F_2 \pm (\ 3G_2 + 36G_4) \\ {}^1F, {}^3F &= F_0 - 15F_2 \mp (15G_2 - \ 9G_4) \\ {}^1G, {}^3G &= F_0 + \ 5F_2 \pm (45G_2 + \ G_4). \end{aligned} \qquad (pf)$$

The formulas for df are

$$\begin{aligned} {}^1P, {}^3P &= F_0 + 24F_2 + 66F_4 \pm (\ G_1 + 24G_3 + 330G_5) \\ {}^1D, {}^3D &= F_0 + \ 6F_2 - 99F_4 \mp (\ 3G_1 + 42G_3 - 165G_5) \\ {}^1F, {}^3F &= F_0 - 11F_2 + 66F_4 \pm (\ 6G_1 + 19G_3 + \ 55G_5) \\ {}^1G, {}^3G &= F_0 - 15F_2 - 22F_4 \mp (10G_1 - 35G_3 - \ 11G_5) \\ {}^1H, {}^3H &= F_0 + 10F_2 + \ 3F_4 \pm (15G_1 + 10G_3 + \ G_5). \end{aligned} \qquad (df)$$

Finally the formulas for two non-equivalent f electrons are

$$\begin{aligned} {}^1S, {}^3S &= F_0 + 60F_2 + 198F_4 + 1716F_6 \pm (G_0 + 60G_2 + 198G_4 + 1716G_6) \\ {}^1P, {}^3P &= F_0 + 45F_2 + \ 33F_4 - 1287F_6 \mp (G_0 + 45G_2 + \ 33G_4 - 1287G_6) \\ {}^1D, {}^3D &= F_0 + 19F_2 - \ 99F_4 + \ 715F_6 \pm (G_0 + 19G_2 - \ 99G_4 + \ 715G_6) \\ {}^1F, {}^3F &= F_0 - 10F_2 - \ 33F_4 - \ 286F_6 \mp (G_0 - 10G_2 - \ 33G_4 - \ 286G_6) \\ {}^1G, {}^3G &= F_0 - 30F_2 + \ 97F_4 + \ \ 78F_6 \pm (G_0 - 30G_2 + \ 97G_4 + \ \ 78G_6) \\ {}^1H, {}^3H &= F_0 - 25F_2 - \ 51F_4 - \ \ 13F_6 \mp (G_0 - 25G_2 - \ 51G_4 - \ \ 13G_6) \\ {}^1I, {}^3I &= F_0 + 25F_2 + \ \ 9F_4 + \ \ \ F_6 \pm (G_0 + 25G_2 + \ \ 9G_4 + \ \ \ G_6), \end{aligned} \qquad (ff)$$

from which the values for f^2 can be obtained by ignoring the part involving G integrals and remembering that the allowed terms are ^1S, ^3P, ^1D, ^3F, ^1G, ^3H and ^1I.

The most striking thing about these results perhaps is the uniform way in which an alternation of the relative height of singlet and triplet is predicted, since in most cases the G of lowest index will be enough larger than the others to dominate the whole expression in the G's. Russell and Meggers[5] called attention to this alternation in 1927 and "commended it to the attention of theoretical investigators." Its explanation by the quantum mechanics must be counted as an important success for the theory.

[5] Russell and Meggers, Sci. Papers Bur. Stand. **22**, 364 (1927).

§4. Three-Electron Configurations

It would be a waste of time to work out all possible three-electron configurations at present, therefore we confine ourselves to cases for which we have been able to find experimental data with which to check the results. The addition of an s electron to p^2, d^2 or pd gives three important cases.

According to the vector coupling viewpoint the addition of an s electron to p^2 gives the results $^1S\rightarrow{}^2S$, $^3P\rightarrow{}^2P$ and ^4P, and $^1D\rightarrow{}^2D$. In the formulas for p^2s the F integrals are of the type $F(np^2)$ while there now appears a G integral to represent the action of the s electron, which is $G_1(np, n's)$:

$$\begin{aligned} {}^2S &= F_0 + 10F_2 - G_1 \\ {}^2P &= F_0 - 5F_2 + G_1 \\ {}^4P &= F_0 - 5F_2 - 2G_1 \\ {}^2D &= F_0 + F_2 - G_1 \end{aligned} \qquad (p^2s)$$

where $F_0=2F_0(np, n's)+F_0(np^2)$. Thus $3G_1$ is the $^2P-{}^4P$ interval and the quantities ^2S, $(^2P+2{}^4P)/3$ (which is the center of gravity of this combination), and ^2D have the same intervals as ^1S, ^3P and ^1D in p^2.

Similar results hold for d^2s. Here too the singlets of d^2 become doublets and the triplets split into doublets and quartets:

$$\begin{aligned} {}^2S &= F_0 + 14F_2 + 126F_4 - G_2 \\ {}^2P &= F_0 + 7F_2 - 84F_4 + G_2 \\ {}^4P &= F_0 + 7F_2 - 84F_4 - 2G_2 \\ {}^2D &= F_0 - 3F_2 + 36F_4 - G_2 \\ {}^2F &= F_0 - 8F_2 - 9F_4 + G_2 \\ {}^4F &= F_0 - 8F_2 - 9F_4 - 2G_2 \\ {}^2G &= F_0 + 4F_2 + F_4 - G_2 \end{aligned} \qquad (d^2s)$$

in which

$$\begin{aligned} F_0 &= F_0(nd^2) + 2F_0(nd, n's) \\ G_2 &= G_2(nd, n's). \end{aligned}$$

The relation to d^2 is evident on comparison. Further we see that the doublet-quartet interval is the same for the P and the F multiplets, being equal to $3G_2$.

In the case of pds we encounter the first instance in which it is impossible to get complete formulas by Slater's diagonal sum method since this configuration gives two different ^2P, ^2D and ^2F. This comes about because pd gives $^{1,3}P,D,F$ and the added s electron makes the singlets into $^2P,D,F$, and splits each triplet into $^{2,4}P,D,F$. In such a case the method gives simply the arithmetic mean of the two doublets of similar L value:

$$\begin{aligned} (^2P) &= F_0 + 7F_2 \\ {}^4P &= F_0 + 7F_2 - (G_1{}^{pd} + 63G_3{}^{pd}) - G_1{}^{sp} - G_2{}^{sd} \end{aligned}$$

$$
\begin{aligned}
(^2D) &= F_0 - 7F_2 \\
^4D &= F_0 - 7F_2 + (3G_1^{pd} - 21G_3^{pd}) - G_1^{sp} - G_2^{sd} \\
(^2F) &= F_0 + 2F_2 \\
^4F &= F_0 + 2F_2 - (6G_1^{pd} + 3\,G_3^{pd}) - G_1^{sp} - G_2^{sd}
\end{aligned} \qquad (spd)
$$

in which (^2P) indicates the mean of the two ^2P's and

$$
\begin{aligned}
F_0 &= F_0(ns, n'p) + F_0(ns, n''d) + F_0(n'p, n''d) \\
F_2 &= F_2(n'p, n''d) \\
G_1^{sp} &= G_1(ns, n'p) \qquad G_2^{sd} = G_2(ns, n''d) \\
G_1^{pd} &= G_1(n'p, n''d) \qquad G_3^{pd} = G_3(n'p, n''d).
\end{aligned}
$$

Slater has worked out p^3, the result being that the energies increase in the order ^4S, ^2D, ^2P and the interval $(^2P-{}^2D)$ is to $(^2D-{}^4S)$ as 2:3.

For the configuration d^3 we find the energy levels to be,

$$
\begin{aligned}
^2P &= 3F_0 - 6F_2 - 12F_4 \\
^4P &= 3F_0 - 147F_4 \\
(^2D) &= 3F_0 + 5F_2 + 3F_4 \\
^2F &= 3F_0 + 9F_2 - 87F_4 \\
^4F &= 3F_0 - 15F_2 - 72F_4 \\
^2G &= 3F_0 - 11F_2 + 13F_4 \\
^2H &= 3F_0 - 6F_2 - 12F_4
\end{aligned} \qquad (d^3)
$$

where (^2D) indicates the mean of the two ^2D's.

§5. Comparison with Experimental Data, Configurations with p Electrons

The simplest case for comparison with the data is p^2, where the theory predicts that the multiplets come in the order ^3P, ^1D, ^1S, as Slater noted. From

Table III. *p^2 configurations*

Element	Config.	$(^1S-{}^1D)/(^1D-{}^3P)$	Reference
Theory		1.500	
C I	$2p^2$	1.13	1
N II	"	5. (? on ^1S)	2
O III	"	1.14	2
Si I	$3p^2$	1.48	3
Ca I	$4p^2$	−0.01	4
Ge I	"	1.50	5
Sn I	$5p^2$	1.39	5
Pb I	$6p^2$	0.62	6
Bi II	"	0.51	7

[1] Paschen and Kruger, Ann. d. Physik **7**, 1 (1930).
[2] Fowler and Selwyn, Proc. Roy. Soc. **A118**, 42 (1928).
[3] Slater, Phys. Rev. **34**, 1317 (1929).
[4] Russell, Astrophys. J. **66**, 190 (1927).
[5] Rao, Proc. Roy. Soc. **A124**, 475 (1929).
[6] Gieseler and Grotrian, Zeits. f. Physik **39**, 377 (1926); Sur, Phil. Mag. **3**, 736 (1927).
[7] McLennan, McLay, and Crawford, Proc. Roy. Soc. **A129**, 584 (1930).

§3 we see that the ratio $(^1S-{}^1D)/(^1D-{}^3P)=3/2$ according to theory. Slater gives the normal configuration of Si I as an example, and we find several more, as given in Table III.

From this it would appear that some influence depresses the ^1S in general, and that the doubtful ^1S given by Fowler and Selwyn for N II is probably wrong. Pb I and Bi II are so far from Russell-Saunders coupling that a good fit would hardly be expected.

The configurations p^3 and p^4 may be discussed here because they are similar to p^2. For p^3 the theory says that the ratio $(^2P-{}^2D)/(^2D-{}^4S)$ equals 2/3. Table IV gives the known instances.

TABLE IV. p^3 *configurations*

Element	Config.	$(^2P-{}^2D)/(^2D-{}^4S)$	Reference
Theory		0.67	
N I	$2p^3$	0.50	1
O II	"	0.51	2
F III*	"	0.46	3
S II	$3p^3$	0.65	4
As I	$4p^3$	0.72	5
Sb I	$5p^3$	0.91	6
Bi I	$6p^3$	1.12	6

[1] Compton and Boyce, Phys. Rev. **33,** 147 (1929); Ekefors, Zeits. f. Physik **63,** 442 (1930).
[2] Russell, Phys. Rev. **31,** 27 (1928).
[3] Dingle, Proc. Roy. Soc. **A122,** 144 (1929).
[4] Ingram, Phys. Rev. **32,** 172 (1928); L. and E. Bloch, C. R. **188,** 160 (1929).
[5] Rao, Proc. Roy. Soc. **A125,** 240 (1929).
[6] Charola, Phys. Zeits. **31,** 458 (1930).
* No intercombinations are found between the quartet and doublet systems, and the relative term values are probably quite inaccurate.

The continued increase in this ratio as the total quantum number increases is to be noted particularly. The closeness of the ratio for N I and O II would indicate that the ratio for the unreliable F III should perhaps be closer to 0.51.

For p^4 the theory gives the same result as for p^2. Table V gives the examples.

TABLE V. p^4 *configurations*

Element	Config.	$(^1S-{}^1D)/(^1D-{}^3P)$	Reference
Theory		1.50	
O I	$2p^4$	1.14	1
Se I	$4p^4$	1.71	2
Te I	$5p^4$	1.71	2

[1] Frerichs, Phys. Rev. **36,** 398 (1930); Hopfield, Phys. Rev. **37,** 160 (1931).
[2] McLennan and Crawford, Nature **124,** 874 (1929).

The new data of Frerichs show that O I is not in as good agreement with the theory as indicated in one of Slater's examples, his ratio being 1.55. Slater took his data from a remarkable energy-level diagram by McLennan, McLeod and Ruedy, Phil. Mag. **6,** 565 (1928), in which the wave number difference for $^1S-{}^1D$ is given as 39,500, although the main point of the paper is the identification of this transition with the auroral green line!

We have found two complete p^2s configurations, which should be similar to p^2 as indicated in §4. The ratio $(^2S-{}^2D)/(^2D-P)$, where $P=(2^4P+{}^2P)/3$, which should be 1.50, is 0.58 in As I[6] and 3.58 in Sb III.[7]

pp, *pd*, and *pf* give similar triads, in which the means of singlet and triplet should lie in the corresponding orders: *P D S*, *D F P*, *F G D*, lowest energy first, with the ratios $(S-D)/(D-P)=9/6$; $(P-F)/(F-D)=5/9$; $(D-G)/(G-F)=7/20$, respectively.

We have found the *pp* complete only for C I[8], N II[9], and O III[10], but since these all occur with the means in the wrong order we do not give the details.

This failure of C I, N II, and O III to agree with the theory appears also in the known *pd* configurations, the mean of the *F*'s being low in every case.[8,9,10] Yt II,[11] La II,[12] and Ge I[13] $4p5d$, also have the *pd* means in the wrong order. The means of Ge I $4p4d$, and Zr III $5p4d$[14] come in the right order with the ratio $(P-F)/(F-D)$, which is theoretically 0.555, having the value 0.28 and 3.58, respectively. More interesting is the behavior of $4p3d$ in the isoelectronic sequence Ca I[15], Sc II[16], Ti III[17], V IV[18] and Cr V[18]. The first two come in the wrong order, giving $(P-F)/(F-D)=-0.15$ and -0.06, respectively, but the last three agree satisfactorily, the ratios being $+0.45$, 0.49, and 0.548. Since $P-F=10F_2(4p3d)$ and $F-D=18F_2(4p3d)$, we can get two values of F_2 for each of these last three ions. Taking the average of these two, we have $F_2(4p3d)$ for Ti III, 427; V IV, 569; Cr V, 707 cm^{-1}. These are perfectly linear, as shown by the plot in Fig. 2, together with corresponding *F*'s for d^2. We have a further check on the three singlet-triplet separations in terms of the two parameters G_1 and G_3, which it is fruitless to apply to the cases in which the means fitted poorly, but interesting in the other three cases.

TABLE VI. *3p 4d singlet-triplet separations*

	Ti III		V IV		Cr V	
	obs.	calc.	obs.	calc.	obs.	calc.
$^1P-{}^3P$	2810	2785	4761	4873	6894	7208
$^1D-{}^3D$	−2056	−1970	−1588	−1935	− 826	−1704
$^1F-{}^3F$	5270	5310	6784	6590	8161	7648
G_1	435		534		614	
G_3	15.2		30.2		47.4	
G^1	6520		8000		9200	
G^3	3720		7400		11600	

[6] Rao, Proc. Roy. Soc. **A125,** 240 (1929).
[7] Lang, Phys. Rev. **35,** 445 (1930).
[8] Paschen and Kruger, Ann. d. Physik **7,** 1 (1930).
[9] Ingram, Phys. Rev. **34,** 427 (1929).
[10] Fowler and Selwyn, Proc. Roy. Soc. **A118,** 42 (1928).
[11] Meggers and Russell, B. S. Jl. of Res. **2,** 733 (1929).
[12] Meggers and Russell, see §7.
[13] Rao, Proc. Roy. Soc. **A124,** 467 (1929).
[14] Kiess and Lang, B. S. Jl. of Res. **5,** 311 (1930).
[15] Russell, Astrophys. J. **66,** 190 (1927).
[16] Russell and Meggers, Sci. Papers Bur. Stand. **22,** 329 (1927).
[17] Russell and Lang, Astrophys. J. **66,** 19 (1927).
[18] White, Phys. Rev. **33,** 542 (1929).

Ti III, V IV and Cr V all alternate properly, as pointed out in §3. Table VI shows the results of fitting the data to the formulas for the separations by least squares.

It is seen that, in the opposite order from the means, Ti III fits best and V IV next. The G's are again approximately linear functions of the ionic charge. G^3 becomes greater than G^1, which is allowed.

For *pf* in La II[12] the ratio $(D-G)/(G-F)$ is 1.05 instead of the theoretical 0.35.

There is one more instance of a configuration with p electrons in which one gets a determined ratio, namely *pds*. In this case (see §4) nothing can be pre-

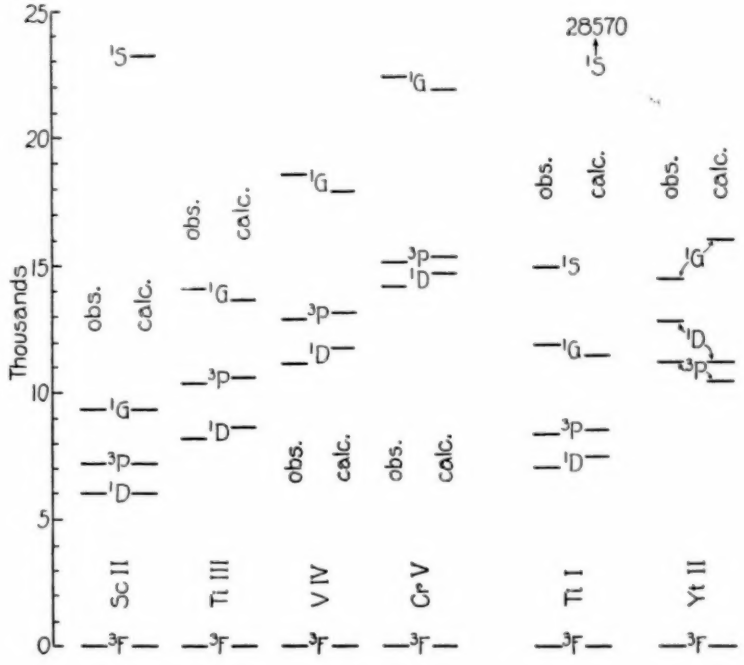

Fig. 1. The configuration d^2.

dicted concerning the quartets, ^4P, ^4D, ^4F; but the theory predicts a constant ratio between the means of the two ^2P's, the two ^2D's, and the two ^2F's which occur. If we designate these means by $P\ D\ F$, we have the order $D\ F\ P$ as in *pd*, with the same ratio $(P-F)/(F-D)=5/9$. In Sc I[16] these means have the wrong order, $D\ P\ F$; and in Yt I[11] and Zr II[19] the above ratio has the values 1.86 and 2.08, respectively, much too large.

In general the predictions of the theory have been seen to fit very poorly for configurations with p electrons, a uniform trend having been observed in p^3, and good fits having been obtained for *pd* in the higher members of the CaI isoelectronic sequence.

[19] Kiess and Kiess, B. S. Jl. of Res. **5**, 1210 (1930).

§6. Comparison with Experimental Data, d Electrons

For d^2 the theory predicts (see §3) the energies of the five multiplets ^1S, ^3P, ^1D, ^3F, ^1G in terms of three integrals, the ^1S being predicted extremely high. In no instance, where a ^1S is reported, is it anywhere nearly high enough, and so we have investigated the other four levels, making a least-squares fit of the separations of ^3P, ^1D, ^1G from the low ^3F, which three separations the theory gives in terms of the two parameters F_2 and F_4.

In the isoelectronic sequence Sc II[16], Ti III[17], V IV[18], and Cr V[18], it was found possible to make the excellent fits plotted in Fig. 1 for $3d^2$. The predicted height of ^1S in Sc II is shown, the other ^1S's being correspondingly high. Russell and Meggers reported a ^1S between the ^1D and ^3P of Sc II, but later, in a note to their Yt paper[11] they ascribe this not to $3d^2$ but to $4s^2$. The $3d^2\ ^1S$ as predicted would be in the midst of the configuration $4p3d$ with which they get their strong combinations, and so difficult to find. In Ti III, Russell

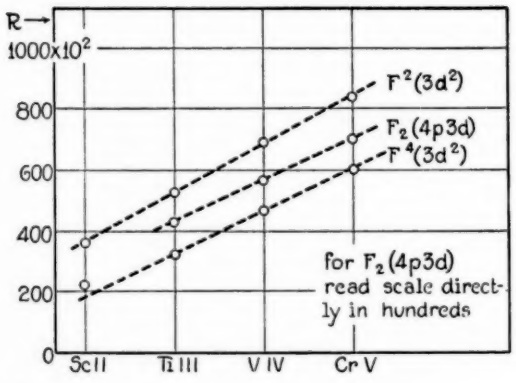

Fig. 2. Values of some integrals for the Ca I isoelectronic sequence.

and Lang report a ^1S just under the ^1G, but with a question mark. This undoubtedly does not belong to $3d^2$. In V IV and Cr V, White reports a ^1S just above the ^1G, but since these spectra were analyzed practically by extrapolation from Sc II and Ti III these levels also are probably not part of $3d^2$. The values of F^2 and F^4 as determined in this way show a striking linearity as plotted in Fig. 2. Slater's $F^2(3d^2)$ and $F^4(3d^2)$ are plotted in place of our F_2 and F_4 in order to show their relative magnitudes. Table VII gives these values ($D_2=49$, $D_4=441$):

Table VII.

	Sc II	Ti III	V IV	Cr V
$F^2(3d^2)$	36180	52840	69300	84330
$F^4(3d^2)$	22740	32520	47020	60880

These values are in good accord with Slater's rough estimate that F^4 is approximately half of F^2.

Russell[20] has completed the $3d^2$ also in Ti I, the levels being shown in Fig. 1, together with the theoretical levels with $F_2(3d^2)=899.5$ and $F_4(3d^2)=66.15$. This is again an excellent fit except for ^1S, as was pointed out by Slater. Meggers and Russell[11] have found all but the ^1S in the $4d^2$ of Yt II, but here, see Fig. 1, not a very good fit is obtained of the rest of the levels, although the perturbations are not great. This plot is made with $F_2(4d^2)=625.2$ and $F_4(4d^2)=55.1$.

In contrast to these reasonable fits we have the Zr III $4d^2$ of Kiess and Lang,[14] in which not only is the ^1S much too low, but the *two* intervals between *no three* of the other levels may be fitted with possible values of the *two* parameters F_2 and F_4; either it is necessary to assume that one of the integrals is

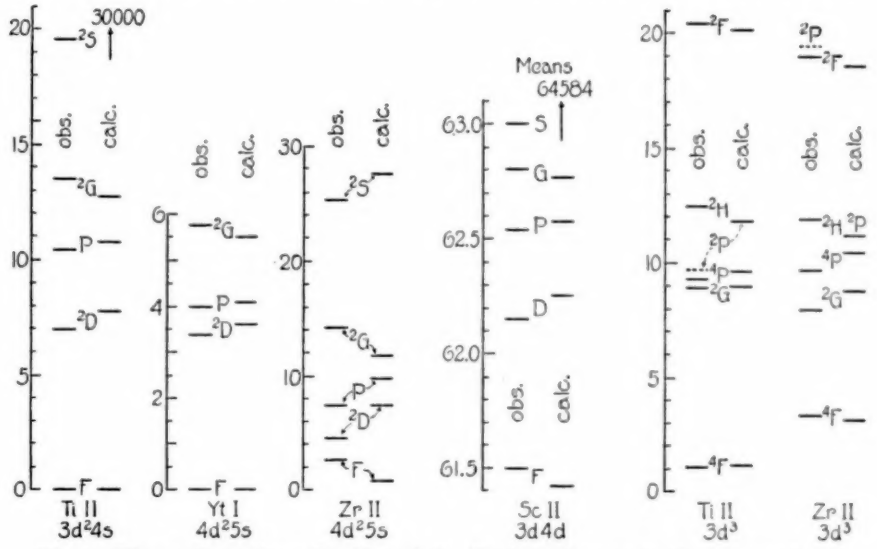

Fig. 3. The configurations d^2s, dd, and d^3. (Scale in thousands of wave numbers.)

negative or that F^4 is many times greater than F^2. In the $5d^2$ of La II (see §7 for energy levels) we have a somewhat different situation. No ^1S is reported, and of the four remaining levels there are three, and just three, which may be fitted with possible values of the parameters. These are ^3P, ^3F, ^1G with $F_2=495$ and $F_4=35.4$. (The two parameters fit the two intervals exactly, of course.) This leaves the ^1D almost 5000 cm^{-1} too high.

In d^2s we have exactly the same situation as in d^2 when we take the weighted means of ^2P and ^4P, and ^2F and ^4F, as analogous to ^3P and ^3F, respectively. Here again we can get good least squares fits of the F, ^2D, P, ^2G levels of $3d^24s$ of Ti II[21] and $4d^25s$ of Yt I[11]. These are plotted in Fig. 3. In Ti II a ^2S is observed at about the same relative position as the ^1S of Ti I, while calculated it should be much higher. Again in Yt I no ^2S is observed. The values of the parameters are, for Ti II, $F_2=1014.7$, $F_4=59.2$ and for Yt I, $F_2=433.6$, $F_4=32.1$. We have $F^2=1.91F^4$ and $1.51F^4$ respectively in these

[20] Russell, Astrophys. J. **66**, 347 (1927).
[21] Russell, Astrophys. J. **66**, 283 (1927).

two cases. In Zr II[19], $4d^25s$, we have the first instance in which a ^2S is found reasonably high. In this configuration, although we cannot get a very good fit, in contrast to the $4d^2$ of Zr III almost any three of the five levels will give reasonable values of the parameters, and we can get an approximate fit of all five by taking $F_2=905$, $F_4=55$ as indicated in Fig. 3 ($F_0-G_2=8000$ cm^{-1} measured from Kiess and Kiess' low $^4F_{1\frac{1}{2}}$, see §3). The fit would not be much improved by omitting any one of the multiplets from consideration so here we have probably a generally large second order perturbation. We have a further check in this configuration on the doublet-quartet separations, which should be the same for P and F terms, being equal to $3G_2$. We have for Ti II, $^2P-^4P=6620$, $^2F-^4F=4558$; and for Yt I, $^2P-^4P=3964$, $^2F-^4E=4357$. These show reasonable agreements, but Zr II is badly off, for here we have $^2P-^4P=-1877$, and $^2F-^4F=+5404$.

The *dd* configuration gives us a pentad, $^{1,3}SPDFG$, with three F's to fit the means and three G's to fit the separations. The first and best instance of this configuration is the Sc II $3d4d$ of Russell and Meggers.[16] Here we can fit the $PDFG$ means as shown in Fig. 3 using $F_2(3d4d)=107$, $F_4(3d4d)=6$ ($F_0=62330$). The S mean is observed some 1600 cm^{-1} too low, which could be caused by the ^1S being about 3000 cm^{-1} too low. When we consider the separations (*singlet−triplet*) we find that we can obtain a fairly good fit of the P D F G separations, with the observed S separation much too small, as shown by Table VIII.

TABLE VIII. *Sc II 3d 4d separations*

	Obs.	Calc.
$^1S-^3S$	3872	6368
$^1P-^3P$	−4275	−4385
$^1D-^3D$	4384	4492
$^1F-^3F$	−3935	−3810
$^1G-^3G$	4864	4760

These are calculated using $G_0=2230$, $G_2=36.7$ and $G_4=3.5$, making $G^0(3d4d)=2230$, $G^2(3d4d)=1800$, $G^4(3d4d)=1540$. (The G^0, unlike F^0, carries here its full meaning as an integral.) The S separation is about 2500 cm^{-1} too small, which would indicate a ^1S about that much too low. This is in good agreement with the predictions of the calculation of the means and indicates that this ^1S is perhaps incorrect, the correct one being some 2500–3000 cm^{-1} higher. An error in the assignment of a singlet term, especially a ^1S, is quite likely to occur, since the identification of such terms is very difficult. An interesting example of this sort will be discussed in §7.

The other instances of the *dd* configuration are not as good. Of the $4d5d$ of Yt II[11], no *three* of the means will fit with reasonable values of F_2 and F_4, the D and the S in particular being very low. Since the S separation was also large and negative where the theory, by comparison with the other separations, says it should be positive, Professor Russell assigned the 61367 ^1S to $4d5d$, discovering that the 59615 level he had assigned was not real; but this still is perhaps not the right level, since we have now a separation of only

+167 whereas the S separation should probably be a great deal larger. The other levels do not fit well enough to say anything definite. In the $4d5d$ of Zr III[14], Kiess and Lang do not find a ^1G, but of the means of the $S\ P\ D\ F$ singlets and triplets, no three will fit with positive values of F_2. Of the La II[12] $5d6d$ means the $P\ D\ F\ G$ will fit very well, with $F_2=115$, $F_4=4$ ($F_0=54430$), with the S much too low, as in the case of Sc II, but this fit is not borne out by the separations, which are entirely skew, the P separation even being -2176 when it should probably be positive.

The other d configuration which we have found almost complete is d^3. Here we get ^2PFGH, ^4PF, and two ^2D's. Russell[21] in Ti II $3d^3$, has found all but one ^2D, and Kiess and Kiess have found all the multiplets of the $4d^3$ of Zr II.[19] The theory predicts, surprisingly, that ^2H and ^2P should have the same energy. Of these, in our two instances, the ^2H fits well, but the ^2P is considerably separated from it. Of the two ^2D's only the mean is given by the theory, but in Zr II this comes far from fitting well. However, in both cases we can fit the other five levels, ^2FGH and ^4PF surprisingly well with our three

TABLE IX. *La II*

$6s^2$	
^1S	7473
$6s6p$	
^1P	45692
^3P	32699
$6s5d$	
^1D	1394
^3D	2760
$6s4f$	
^1F	15773
^3F	14888
$6p^2$	
^1S	66592
^3P	61779
^1D	62026
$6p5d$	
^1P	30353
^3P	28833
^1D	24462
^3D	27538
^1F	32201
^3F	27477
$6p4f$	
^1D	40458
^3D	38835
^1F	37210
^3F	37034
^1G	39221
^3G	37479
$5d^2$	
^1S	—
^3P	5949
^1D	10095
^3F	1183
^1G	7473
$5d6d$	
^1S	54794
^3S	55230
^1P	56037
^3P	53861
^1D	55184[1]
^3D	53067
^1F	52138?
^3F	54819[1]
^1G	56036
^3G	53659
$5d4f$	
^1P	27424
^3P	23003
^1D	18895
^3D	22174
^1F	24523
^3F	18411
^1G	16599
^3G	21478
^1H	28525
^3H	18835
$4f^2$	
^1S	69505
^3P	63960
^1D	59900
^3F	57939
^1G	59528
^3H	56080
^1I	62408

[1] The $^1D_2$ and $^3F_2$ of the $5d6d$ may possibly be interchanged. ($^3F_4=55321$, $^3F_3=54840$, $^3F_2=53885$.)

parameters, as indicated in Fig. 3. For Ti II we have $F_2(3d^2) = 845$, $F_4(3d^2) = 54$ ($3F_0 = 17750$); corresponding to $F^2 = 1.74F^4$. The mean of the ^2D's is predicted at 22140, which would throw the ^2D not found at about 31000, very high indeed. For Zr II we have $F_2 = 683$, $F_4 = 36$ ($3F_0 = 16000$); corresponding to $F^2 = 2.11F^4$. The mean of the ^2D's is predicted at 19523, observed at 14214 (multiplets at 13869 and 14559).

We have seen that the theory works much better for d electrons than for p. It has been good in every instance in the first long period of the periodic table, and better in the second than the third.

§7. La II and the f Electron Configurations

W. F. Meggers and H. N. Russell have recently completed the analysis of La II, obtaining the first complete pf, df and f^2 configurations. Through their kindness in allowing us to use these data we have been able to obtain two beautiful fits of the df and f^2 configurations, and to prove the actual service of this theory to spectroscopists by helping to straighten out the analysis at two or three points.

Since these data are unpublished as yet, Meggers and Russell have kindly allowed us to publish a preliminary energy table, the levels being measured up from the low $5d^2\ ^3F_2$. We give only the centers of gravity of the multiplets in Table IX.

Of these the p^2, pd, pf, d^2, and dd have already been discussed, and were not found to agree particularly well with the theory. The new $5d4f$ and $4f^2$ remain to be considered, which will be done in some detail.

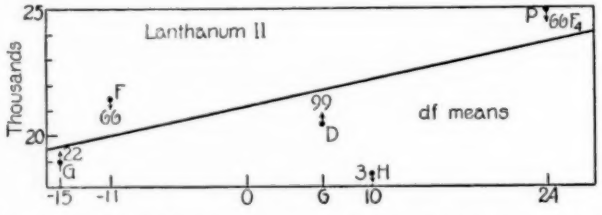

Fig. 4. Illustrating the method of locating poorly fitting multiplets and a method of estimating the values of the integrals.

As we received the data from Professor Russell, the $df\ ^1H$ was placed at 18169, rather close to ^3H, instead of having the extremely great separation of about 10,000 units and being the highest level in the configuration. An attempt to fit the means by the method illustrated in Fig. 4 was made. This is incidentally the method used on many of the previous configurations. The formulas to which we are fitting these means are as follows:

		Calc.
P = 25214	$= F_0 + 24F_2 + 66F_4$	25216
D = 20534	$= F_0 + 6F_2 - 99F_4$	20506
F = 21467	$= F_0 - 11F_2 + 66F_4$	21191
G = 19038	$= F_0 - 15F_2 - 22F_4$	19323
H = 18502	$= F_0 + 10F_2 + 3F_4$	22598

Since F_0 occurs uniformly, we plot in Fig. 4 the value of these means against the coefficients of F_2. Then the line determining F_2 must be so drawn that its separations from these points are as closely as possible proportional to the coefficients of F_4 and in the direction shown by the arrows. It is seen at once that we can thus fit G,F,D, and P quite well, but that H is far too low. From the slope of the line we get $F_2=115$, from the average separations $F_4=16$ (and from the height at zero abscissa, $F_0=21400$). From the level diagram in Fig. 5 we see that changing none of these values will tend to improve the general fit, so that these are approximately as good as can be found. A more exact determination of these values, such as a least squares fit, gives an accuracy which is meaningless. The calculated means are shown in the above table. From the calculated H mean it would seem that the ^1H should be about 8200 units higher.

When we consider the separations we have the following formulas to determine the G's

			Calc.
$^1P - {}^3P$	$= -4421$	$= -2(\ G_1 + 24G_3 + 330G_5)$	-4638
$^1D - {}^3D$	$= 3279$	$= 2(\ 3G_1 + 42G_3 - 165G_5)$	3397
$^1F - {}^3F$	$= -6112$	$= -2(\ 6G_1 + 19G_3 + 55G_5)$	-5837
$^1G - {}^3G$	$= 4879$	$= 2(10G_1 - 35G_3 - 11G_5)$	4987
$^1H - {}^3H$	$= +666$	$= -2(15G_1 + 10G_3 + G_5)$	-11330

It is inconvenient here to use such a method of fitting as described above, but such a diagram will readily show that the H separation relative to the others should be very large and negative. A least squares fit of the $P\ D\ F\ G$ separations gives $G_1=357.6$, $G_3=29.7$, $G_5=3.78$, and the calculated separations show in the table, a good fit. These values correspond to $G^1(5d4f)=12{,}500$, $G^3=9350$, $G^5=5750$. This calculation shows that the ^1H should be about 12,000 units higher.

In the data as received from Professor Russell, the $4f^2\,^1I$ was placed at 52,052 instead of the value noted in the table, and two possibilities given for ^1S and ^1D, as noted below. The f^2 consists of seven levels to be fitted with four parameters as follows:

$$^1S = \begin{Bmatrix} 69505 \\ 66592 \end{Bmatrix} = F_0 + 60F_2 + 198F_4 + 1716F_6$$

$$^3P = 63963 = F_0 + 45F_2 + 33F_4 - 1287F_6$$

$$^1D = \begin{Bmatrix} 59900 \\ 62026 \end{Bmatrix} = F_0 + 19F_2 - 99F_4 + 715F_6$$

$$^3F = 57939 = F_0 - 10F_2 - 33F_4 - 286F_6$$

$$^1G = 59528 = F_0 - 30F_2 + 97F_4 + 78F_6$$

$$^3H = 56080 = F_0 - 25F_2 - 51F_4 - 13F_6$$

$$^1I = 52052 = F_0 + 25F_2 + 9F_4 + F_6.$$

Now from a diagram such as Fig. 4, it may be seen that F_6 will be extremely small, for a good fit of the high ^1S, the low ^1D, the ^3P, ^3F, ^1G, and ^3H may be obtained using just the parameters $F_2=94.0$, $F_4=22.1$. The ^1I is definitely observed 10000 units too low. The correct ^1S and ^1D are at once determined, since the other possibilities will not fit under any circumstances.

Thus we have seen that the theory predicted the ^1H of df and the ^1I of f^2 both about 10,000 units higher, and when this was called to the attention of Professor Russell, he discovered that he could make this shift by rearranging his lines as shown in Fig. 6. Upon doing this he immediately was able to check each of these levels by faint cross-combination lines, thus definitely proving

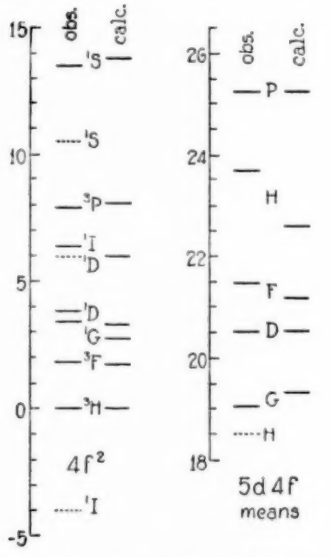

Fig. 5. The configurations df and f^2 of La II. (Scale in thousands of wave numbers.)

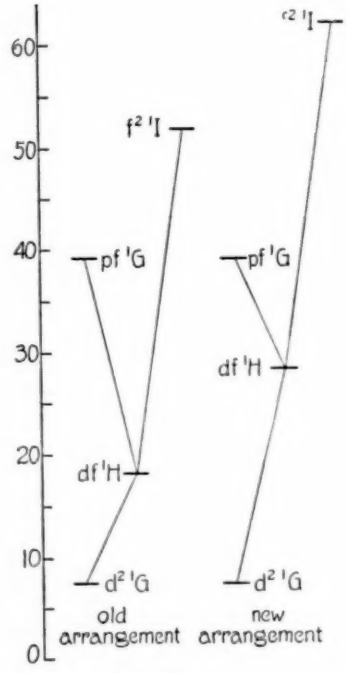

Fig. 6. Russell's rearrangement of the La II singlets according to the predictions of the theory. (Scale in thousands of wave numbers.)

the correctness of this arrangement. Both of these singlets were raised 10,356 units to the places shown in Table IX. In Fig. 5, the old levels are shown broken and the corrected levels by full lines. The df diagram is merely the old diagram determined from the means of $P\ D\ F\ G$, with the H mean put in its proper place. The $^1H-^3H$ separation becomes now 9690 against the calculated 11330 from the other four separations. The ^1H was raised just about the average of the predictions from the means and from the separations. It is supposed that the $3d4d\,^1S$ of Sc II would behave in about this fashion. For the f^2 the ^1I is placed within 300 units of its prediction using the two coefficients above. Fig. 5, however, is a recalculation using least squares to fit the three

coefficients F_2, F_4, F_6 to the separations of all the levels from the low ^3H. This gives a surprisingly good fit of the 6 intervals in terms of the 3 integrals, with the value of $F^2=21{,}000$, $F^4=23{,}500$, $F^6=1930$. Unfortunately F^4 comes out a little larger than F^2 whereas it must be smaller.

Thus we have obtained quite pleasing results with these two f-electron instances, the theory having stood the test of prediction and been of actual service in the analysis of the spectrum, both in the assignment of ^1S and ^1D, f^2, the former of which Professor Russell says he had little possibility of assigning definitely, and in the rearrangement of the levels in both df and f^2.

Kiess and Lang[14] have completed the $4d4f$ configuration of Zr III except for the ^3H, but when the other four means are plotted as in Fig. 4, it is seen that no three of them will fit in any fashion. The P, D, and F separations alternate but the G does not.

In conclusion we may say that this first approximation seems to be most accurate for those configurations with lowest total quantum numbers in comparison with the angular momentum quantum numbers, the $3d$ and $4f$ in particular giving good results.

We wish to thank Professor H. N. Russell for his helpful interest in this work, and him and Dr. Meggers for permission to publish their lanthanum data.

DENSITY AND CONDUCTIVITY OF BISMUTH SINGLE CRYSTALS GROWN IN MAGNETIC FIELDS WITH RELATION TO THEIR MOSAIC STRUCTURE

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Abstract

In continuation of the study of the thermoelectric effect, previously described by Goetz and Hasler, existing between the two halves of the same bismuth single crystal, of which one has been crystallized within, and the other outside of a strong magnetic field (21,000 gauss), the density and the specific resistance of different sections of these crystals, grown by the discontinuous method, have now been measured.

The change of density of "magnetic" crystals. The density of perfect crystals grown under normal conditions was found to be between 9.82 and 9.83 i.e., 0.2 percent higher than the values of other authors. Furthermore, it was found that any crystalline imperfection such as twinning, etc., decreases the density; that, further there exists a difference of density between the "normal" and the "magnetic" half of the same crystal, the sign of which depends on the orientation with which the crystal entered the field: In case the trigonal axis is normal to the axis of the rod and normal to the lines of force, the "magnetic" half shows an increase of density, whereas the opposite is true in case the principal axis is parallel to the rod (and therefore parallel to the direction of growth and to the heat-flow). The difference of density is ca. 0.3 percent but can be several percent in imperfect crystals. The purity of the metal affects the change of the density. The results indicate that the ideally pure metal would not be affected by the magnetic treatment.

The specific resistance of "magnetic" crystals. The values of the specific resistance obtained on "normal" single crystals agree approximately with the results obtained by Bridgman and Kapitza and also with those obtained by spectroscopic analysis. The value of $\rho_{\parallel}/\rho_{\perp}$ was found to be much larger for bismuth, being sensitive to the "magnetic" treatment. There is a small change of resistance between the normal and the magnetic half, depending on the orientation of the crystal to the field. In case the orientation is such as to decrease the density the resistance increases and *vice versa*. The accuracy necessary for the satisfactory quantitative determination of the change could not yet be reached, since the change is of the magnitude of 0.5 percent.

An attempt is made to combine the phenomena of the magnetic effect thus far known. It seems probable that the influence of the magnetic field upon the formation of a crystal consists of a change within the mosaic structure of the lattice. The investigation is being continued.

Introduction

A THERMOELECTRIC effect within one and the same Bi single crystal of which one half had crystallized under normal conditions, the other within a strong transverse magnetic field has recently been described by A. Goetz and M. F. Hasler.[1] It was found that the size as well as the sign of the e.m.f. depends on the orientation of the crystal with respect to the lines of

[1] A. Goetz and M. F. Hasler, Phys. Rev. **36**, 1752 (1930).

force and on the method of growth; also that the e.m.f. depends largely on traces of impurity within the crystal.

Due to the fact that this magnetic effect is altogether new, very little information as to the cause of the observed e.m.f. can be obtained from the observations themselves and accordingly additional measurements of another type have been here undertaken.

Although we realized in advance that the thermoelectric effect would be by far the most sensitive indicator, and other volume effects should be very minute if at all measurable, there seemed to be encouraging indications in the observations of previous authors concerning the density and the electric conductivity of Bi crystals.

The Density of "Magnetic" Bi Crystals

The density of bismuth has been measured very frequently by different authors and it seems quite remarkable that there is no other common element for which the different observers differ so largely though they seem to have worked with great care. A study of the literature[2] shows that the measured density of Bi varies between 9.66 (Marcus, Giebe) and 10.055 (Zavaffiero), a difference of more than 5 percent. There can be no doubt that part of this variation is due to fissures and inclosures of gas within the metal which falsify the measurement of the volume. It is quite remarkable that the average value of a perfect single crystal is far below the maximum density measured on specimens consisting of compressed powder, thus indicating that the bismuth lattice is *not* the closest possible packing of Bi atoms.

For the present measurement of densities the usual hydrostatic method was improved only in that thin transformer oil was used for the immersing liquid instead of water. In the case of water, it was found that shortly after boiling (a process which is necessary to prevent the formation of gas-bubbles on the surface of the specimen) the absorption of air gradually changes the density until saturation is reached again. In case of oil dried artificially this trouble does not occur and its density can be kept constant for months if one works carefully. The density of the oil was measured in a pyknometer.

To reduce the inaccuracies to a minimum, two pieces of equal length were cut out of one crystal, one belonging to the normal, one to the magnetic side of it. It goes without saying that the crystal had to be free of imperfections—these could be tested for by the thermoanalyser[1]—and also that its surface had to be etched in order to free it from any layer of oxide.

But in spite of the care taken in the measurements and in producing the crystals, the results obtained are not as uniform as expected. Furthermore, according to the thermoelectric results, only measurements on crystals of the same orientation and grown by the same method can be compared. Crystals of the P_1 and P_3-type grown by the discontinuous method, have been investigated, since these orientations show the largest magnetic effects, whereas the P_2-type is almost neutral. In addition to this, it was found that even in the

[2] Gmelin's Handbuch der Anorg. Chem. Vol. 8, page 35.

measurement of density only crystals of the same sort of bismuth[2] could be compared. Thus most attention had been paid to crystals of the "B" bismuth due to the large "magnetic" effect observed on it in the thermoelectric measurements.

Results. In toto, the density of 76 different specimens was measured. These belonged to 29 different crystals grown in general especially for these measurements. Of these specimens, 15 were of the orientation P_1, 6 of P_2, 16 of P_3, 2 of P_{1-2}, and 2 of P_{2-3}**. Several specimens of the magnetic (M) and the normal (N) halves of the same crystal were cleaved into several pieces, each being measured separately in order to determine the influence of local irregularities and to reveal the accuracy of the method. Table I shows part of the results obtained. The section "number of measurements" in Table I indicates how many different measurements of the same crystal or of its different parts were taken, each measurement consisting of the necessary number of readings.

TABLE I.

Crystal	Orientation	Kind	Treatment	Density	Number of measurements
48/00/0	P_1	*B*	N	9.820	Two
62/00/0	"	"	"	9.815	One
62/00/0	"	"	M	9.845	Two
65/20/0	"	"	N	9.824 (+)	One
65/20/n (×)	"	"	"	9.818 (++)	"
65/20/g (××)	"	"	"	9.819 (†)	"
65/20/0	"	"	M	9.844 (+)	"
65/20/n (×)	"	"	"	9.849 (++)	"
65/20/g (××)	"	"	"	9.838 (†)	"
73/00/0	"	*C*	N	9.833	"
"	"	"	M	9.827	"
83/21/1	"	*B*	N	9.830	Two
"	"	"	M	9.842	"
49/00/0	P_2	*B*	N	9.822	Three
59/00/0	"	"	N	9.813	One
"	"	"	M	9.813	"
60/00/0	P_{1-2}	"	N	9.807	"
"	"	"	M	9.825	"
49/00/1	P_3	"	N	9.826	"
61/00/0	"	"	N	9.835	Two
"	"	"	M	9.805	"
96/31/1	"	"	N	9.837 (*)	?
"	"	"	M	9.817 (*)	?
96/21/1	"	"	N	9.847 (Δ)	?
"	"	"	M	9.836 (Δ)	?
69/00/0	"	"	N	9.803	One
"	"	"	M	9.781	"
70/00/0	"	"	N	9.809	"
"	"	"	M	9.798	"

(××) The specimen included a small twinned region.
(×) The same specimen after removing the twinned region.
(+) Probable error 0.005
(++) Probable error 0.008
(†) Probable error 0.01
(*) N Field strength 17,000 Gauss
(Δ) N Field strength 13,000 Gauss

** The designation of the latter two orientations indicates mean intermediate orientations between P_1 and P_2 etc.

With regard to the absolute value of the density it is apparent that *the average value for single-crystals is between 9.82 and 9.83*, slightly higher than the result obtained by Kapitza (9.80).[3] This result was checked by measurements made upon normal crystals in distilled water immediately after its separation from the absorbed air.

The density of Bi, generally speaking, appears to be abnormally sensitive to crystallographic imperfections, since polycrystals for instance as well as crystals with large twinned regions showed abnormally low values, this probably being due to the enclosure of gas at the intercrystalline borders, as was verified several times by the microscope. This sensitivity is also indicated by the fact that the highest values of the density on our best crystals (9.83) are still below the value to be expected from the x-ray data (9.86).

Nevertheless the values given in Table I have but relative importance (with the exception of the crystals 48/00/0, 49/00/0 and 49/00/1) since they are obtained in oil, the density of which could not be checked in the pyknometer as accurately as the values taken with the balance, though the accuracy indicated by the data given is justified for one and the same crystal because these values were obtained in immediate succession and under similar conditions.

The measurements thus obtained indicate the following connection between the normal and the "magnetic" part of the same crystal: *If the crystal has an orientation in which the principal axis is normal to the lines of force* (P_1 and P_3) *the density of both halves differs considerably, whereas no change can be found if the axis is parallel to the field.* (P_2).

Furthermore with relation to the first part it is evident that the *density of the "magnetic" half is larger than that of the normal, in case the trigonal axis is normal to the axis of the rod,* (P_1), *whereas the opposite is true if the axis is parallel to the axis of the rod* (P_3).

In intermediate orientations (P_{1-2}) where P_2 is unaffected, the resulting change is the same as it is in the case of P_1, but one should not rely too much upon it, since there exists only the measurement of one crystal (orientation ca. 30°). Concerning the measurement of the crystal 73/00/0 which has the P_1-orientation but consists of the kind *C* (i.e., the purest metal[1]) it is striking that *no change of density could be observed.*

In consideration of the large experimental difficulties connected with density measurements of this kind, one should not put too much stress on the absolute value of the differences of the density between the normal and the "magnetic" parts, since an almost invisible layer of oxide or grease and small enclosures, difficult to detect, affect the results fatally by fogging the whole effect. Thus a number of observations had to be discarded among which were a few whose sign was not in agreement with the above statement. Nevertheless the discarding was done only after it was evident that the crystals were imperfect.

[3] P. Kapitza, Proc. Roy. Soc. **A119,** 358 (1928).

The Electric Resistivity of "Magnetic" Crystals

As soon as it was evident that the growing of crystals in a magnetic field affects their density, it was decided to measure their electric resistivity, since it is well known that these qualities are closely related within the same metal.

There are a number of very exact investigations published concerning this subject (Bridgman,[4] Schneider,[5] Borelius and Lindh,[6] Schubnikow and de Haas[7] and Kapitza[3]). It is made quite certain by Bridgman that the Voigt-Thomson law holds also in case of Bi, whereas concerning the absolute values of the specific resistance, a small discrepancy still remains between the recent authors, a discrepancy which is very probably due to the fact that it is very difficult to obtain bismuth of sufficient purity, or better of equal impurity.

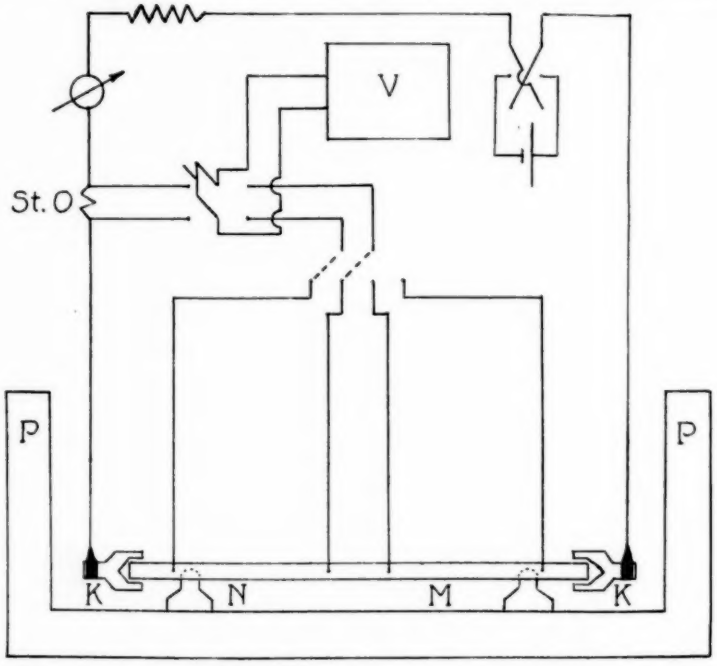

Fig. 1. Diagram of apparatus.

Also the measurements themselves must be performed with special precautions, so as to avoid the large thermoelectric forces due to small changes of temperature as well as any permanent or elastic distortion of the crystal, for these affect the results largely.

We used for our measurements, for the most part, the arrangement already described by Kapitza[3] with certain modifications however, dictated by the much larger size of our crystals and by our special purpose of comparing the values of two different parts of the same crystal. Thus the arrangement was as shown in Fig. 1.

[4] P. W. Bridgman, Proc. Am. Acad. **63,** 351 (1929).
[5] G. W. Schneider, Phys. Rev. **31,** 251 (1928).
[6] G. Borelius and A. E. Lindh, Ann. d. Physik **51,** 607 (1916).
[7] A. Goetz, Phys. Rev. **35,** 193 (1930).

After a crystal of 13 to 15 cm in length, of the desired orientation, was grown within a graphite trough previously described,[7] one half of which (N) was grown under normal conditions, the other (M) within a magnetic field, both ends including the transition between the seed crystal and the main crystal were carefully cleaved off so as to obtain the standard length of 12 cm. Then the crystal was etched and searched for imperfections or twin lamellae. In case it proved satisfactory two copper cups (K)—the current leads—were soldered to the crystal with Wood's metal. This method has the advantage of avoiding the necessity of heating the crystal long enough to produce an alloy between bismuth and Wood's metal, which makes the further use of the bismuth impossible, whereas here one has only to heat the cup filled with Wood's metal up to its melting point and then to put one end of the crystal into it, after which the liquid metal solidifies shrinking around the crystal. Thus a reliable contact for comparatively large currents is made.

The potential leads consisted of 0.1 mm silver wire which was spark-welded on to the crystal at 4 different points as shown in Fig. 1 to allow the measurement of the specific resistance separately across the normal and the magnetic parts of the crystal. In order to keep the temperature constant the whole arrangement was immersed in a bath of oil within a container of paraffin (P).

The current was measured by means of a standard ohm (St. O) and a precision potentiometer V, whereas the voltage across one pair of silver wires was measured directly with the potentiometer. There were furthermore the usual precautions for balancing the thermoelectric effects etc.

The largest difficulty consisted in the exact determination of the cross section of the crystal, since it could not be taken from direct measurement because of the peculiar shape of the trough. Thus it was necessary to calculate the specific resistance from the length (L), the weight (G) and the density (D) by means of the relation:

$$\rho = \frac{E \cdot G}{J \cdot D \cdot L^2}$$

where J and E are current and voltage and ρ the specific resistance. Since it was impossible to obtain any better accuracy by this method than 1—2 percent the variation of density between N and M, as described before, was not considered. For D the value of 9.82 was taken.

The reason for the inaccuracy of this method is found in the assumption that the cross section over the length used is constant. This becomes less true the larger this length is chosen. This distance between the potential leads on the other hand has to be large enough to avoid the influence of the unequal current distribution in the neighborhood of the leads and the uncertainty of the distance due to the cross section of the welding spot, which was in the present case at least 0.5 mm. The distance used was in general between 30 and 40 mm so as to decrease the uncertainty of ρ to about 3 percent.

Results. It is well known that the specific resistance parallel to the trig-

onal axis of a Bi crystal is larger than normal to it, furthermore, that the ratio between these two values increases with the increasing amount of impurity, since in this case, the resistance along the trigonal axis increases faster than perpendicular to it. The minimum values of $\rho_\parallel/\rho_\perp$ are 1.27 (Bridgman[4]) and 1.30 (Kapitza[3]), whereas Schneider[5] finds 1.62 using a metal with 0.04 percent silver. Table II gives the results which seem the most reliable ones. No reliable values for bismuth D^1 could be obtained, since this kind is very hard to obtain in single-crystalline form without inclosed air-bubbles.

TABLE II.

Crystal	Orientation	Kind	Part	Resistance
83/21/1	P_1	B	M+N	1.395
"	"	"	M	1.384
"	"	"	N	1.407
83/11/?	"	"	M+N	1.395
"	"	"	M	1.343
"	"	"	N	1.438
96/31/1	P_3	"	M_1	2.085
"	"	"	M_2	2.088
"	"	"	N_1	2.030
"	"	"	N_2	2.030
91/41/1	P_1	C	M+N	1.109
"	"	"	M	1.122
"	"	"	N	1.090
91/33	P_3	"	N	1.358 (?)
"	"	"	N	1.428
"	"	"	N	1.419
91/51/1	"	"	M+N	1.438
"	"	"	M	1.493
"	"	"	N	1.393
86/11	P_1	A	N	1.334 average
85/21	P_3	"	N	1.745 "

The values for $\rho_\parallel/\rho_\perp$ in Table II are taken at temperature of 25°C which is slightly higher than the temperatures used by Bridgman and Kapitza (20°). This difference makes it necessary to decrease our values about 2 percent to compare them with the values of these authors.

The main reason why our values are not as consistent as Kapitza's and Bridgman's is probably the indeterminancy of the cross section of the crystals. Nevertheless these observations (which are not considered to be final) indicate the following facts.

The variation of the specific resistance of the different kinds of bismuth used is in agreement with the spectroscopic analysis published previously[1] showing that C is the purest metal with a resistance $\rho_\perp = 1.09 \times 10^{-4}$ and $\rho_\parallel$ 1.36(?) to 1.43×10^{-4}. The latter value is slightly larger than Bridgman's (1.38×10^{-4}) but can be easily explained by the lack of longitudinal compression in which case Kapitza obtained values up to 1.5×10^{-4}. Bismuth A can be easily recognized as impure and B is still worse, agreeing with the measurements of Borelius and Lindh. Fig. 2 shows the results for the three different kinds of Bi used; the hatched line below C shows Bridgman's best

values,* the dotted line crossing B gives the conductivity for B crystals grown in the magnetic field in the corresponding orientation, the abscissa is given in the usual terms of $\cos^2$ of the angle of orientation.

The most important fact suggested by the results consists in the influence

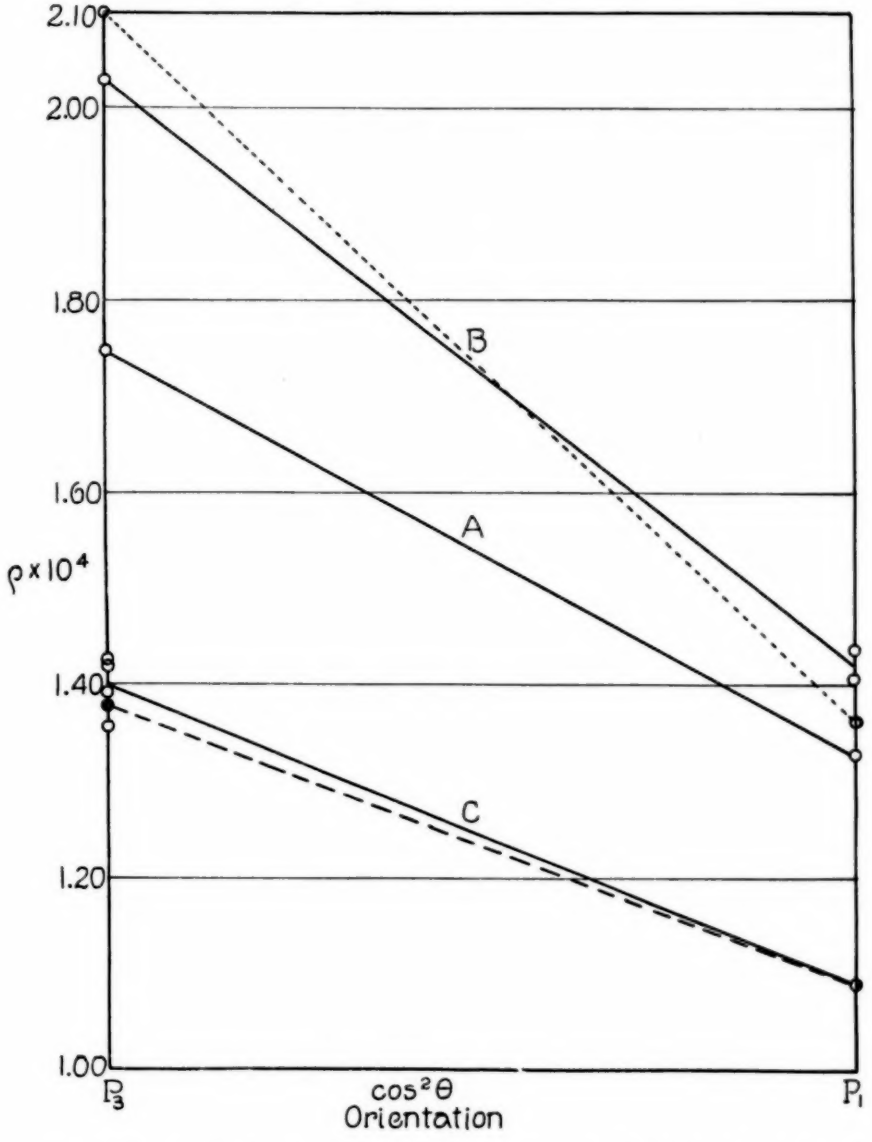

Fig. 2. Results for the three different kinds of Bi used. The hacked line below C shows Bridgman's best values. The dotted line crossing B gives the conductivity for B crystals grown in the magnetic field in the corresponding orientation.

* There is one discrepancy worth mentioning in the fact that Bridgman used Kahlbaum metal which is the same as our D. Kapitza's remark about this metal as well as our analysis shows that it contains a considerable amount of impurity which is different from the con-

the magnetic treatment of the crystal has on the resistance. This runs as follows: *if the crystal has an orientation in which its trigonal axis is normal to the lines of force and normal to the direction of the current the specific resistance of the magnetic half is smaller than the normal one; if the trigonal axis is normal to the lines of force and parallel to the direction of the current the specific resistance of the magnetic half is larger than the normal.*

As to the qualities of the P_2 orientation no exact measurements were yet performed because the thermoanalysis did not show any "magnetic" effect.

Discussion

The results obtained as to the influence of the magnetic field upon the density and the conductivity of Bi single crystals, have a close relation. This is not altogether unexpected. The increase in density is associated with a decrease of specific resistance (P_1) and *vice versa* (P_3). Furthermore, the crystallization within a magnetic field seems to affect the density and conductivity of a metal with small impurities to a much larger extent than a pure one.

Considering the nature of the change within the "magnetic" crystal it is very difficult to say anything that is more than a mere suggestion. Both the thermoelectric effect and the change of conductivity could be explained by a change at the moment of crystallization in the orientation of the crystal when entering a magnetic field. As has been already stated in a previous paper[7] no change in orientation could be detected, furthermore this explanation would account neither for the large influence of impurities nor for the change in density.

Another suggestion would be an allotropic change of the lattice, indicated by the change in density. Hence an x-ray investigation was started after the first indications of a change of density were found. This consisted of Bragg diagrams taken simultaneously from the (111) plane of the normal and the magnetic half of the same crystal, but, as was stated already briefly by Goetz and Hergenrother,[8] not the slightest displacement of corresponding lines was found, thus indicating that *the atomic distance along the trigonal axis does not differ between both parts of the crystal.*

Hence there are obviously only two conclusions left, of which one assumes that the magnetic half undergoes an pseudo-allotropic change of the same type as the $\alpha \rightarrow \beta$-transformation of iron and zinc which cannot be found by x-ray analysis though indicated by electric volume effects. In general one assumes that the transformation of the first metal is only due to an interatomic change of the distribution of electrons and it would be plausible that such an effect occurs more easily if the internal symmetry of the lattice is disturbed by impurities. Nevertheless this suggestion loses probability as it does not account for the change in density in case of Bi.

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tamination of *A* and *B* but much more than *C*. This fact is also indicated by the size of the "magnetic" effect. We were not able to obtain reliable measurements of the specific resistance of this metal whereas Bridgman got the best results yet published.

[8] A. Goetz, R. C. Hergenrother and A. B. Focke, Phys. Rev. **34,** 546 (1929).

Thus there is apparently no mode of explanation left save that which has been suggested in a previous paper as the only way to account for the large effect of minute impurities in a crystal.[1] This way seems indeed to account for the whole phenomenology of these effects, including the change of density and electric conductivity of magnetic Bi crystals. The assumption is of a change in the secondary structure of the crystal as described first by Zwicky.[9,10]

The experimental evidence for the existence of this structure in Bi crystals has already been given by one of the authors.[11] He showed that this structure, superimposed upon the Laue-Bragg lattice, consists of blocks of a definite size which is within the range of microscopic visibility. Our present suggestion is that the arrangement of these blocks is changed under the influence of the magnetic field so as to produce a closer or less close packing. This would not influence the x-ray diagram, since this depends only on the primary structure of the lattice whereas the density of the crystal as a whole would be affected by a change in the mosaic arrangements of the blocks.

This mosaic arrangement of the blocks is thus assumed to be changed by the influence of a field during the formation of the crystal. Such a change, which we have to think of as a systematic distortion, must depend on the crystallographic orientation of the crystal within the field and must disappear if this orientation causes the smallest possible content of free energy upon the crystal as is the case in the P_2 orientation where the direction of the smallest susceptibility is parallel to the lines of force as follows from the measurements of Focke.[12]

This assumption makes it plausible also that the electric conductivity changes with the density, since both depend on the compactness of the crystal.

The hypothesis as a whole implies a less compact form due to the mosaic structure for the average perfect crystal than for an ideal one.** Although it is perhaps possible to think of accidental fissures within the crystal as the cause of the difference between the theoretical and the actual density (0.3 percent), the fact that one can approach the theoretical density by the crystallization in a magnetic field under the same thermal and mechanical conditions of growth seems to be a strong argument against the presence of such fissures dependent upon imperfect growing conditions. Also the consistency of the density values obtained speaks against such an explanation.

Considering the magnitude of the change of density and conductivity in

[9] F. Zwicky, Proc. Nat. Acad. **15,** 253, 816 (1929).

[10] F. Zwicky, Hel. Phys. Acta. **3,** 269 (1930).

[11] A. Goetz, Proc. Nat. Acad. **16,** 99 (1930).

[12] A. B. Focke, Phys. Rev. **36,** 319 (1930).

** This conclusion does not contradict Zwicky's assumption[13] for ionic lattices of Na Cl type, where the actual density of a crystal should be larger than the density calculated from the x-ray diagrams due to the contracted II-planes sandwiched between normally spaced regions. (Hel. acta, page 288.)

magnetic crystals (0.5 percent) one must call these second-order effects in comparison with the magnitude of the thermoelectric changes.[1] This fact also seems to support the suggested hypothesis, since it is well known that thermoelectric effects in general are much more structure-sensitive than density and conductivity known as structure-insensitive.

There are two more arguments in favor of the above explanation: if there is a possibility of a distortion within the mosaic structure, i.e., among the blocks, this can only be possible if during the genesis of the crystal these units possess a larger mobility among themselves than do the molecules of the primary lattice. This is necessary for the following reason: an orienting influence upon the crystal exerted by the magnetic field presupposes the existence of an anisotropic susceptibility. Besides the fact that liquid Bi is almost neutral magnetically and the further fact that the large diamagnetic properties of Bi arise only at the moment* the lattice forms, make it obvious that the magnetic anisotropy cannot exist either before the primary lattice is formed. Hence the orienting influence of the field can only occur if a lattice already exists. As the forces exerted upon the crystal by the fields used are far too small to deform the lattice permanently the only explanation left seems to be the distortion of the secondary structure. This explanation presupposes that the primary structure exists before complete solidification, a fact which former work by one of the authors made highly probable in the case of Bi.[11] The second support of the above hypothesis is found in the observation that a possibility of an orienting influence upon the crystal "*in statu nascendi*" exists in fact, and that it can have mechanical, thermal and

* This statement is not in harmony with Kapitza's hypothesis according to which the large diamagentism of Bi begins only slightly below the melting point after the metal has already solidified. It seems dubious whether this opinion can be supported by Curie's paper on this subject,[14] for he states emphatically: "· · · la chute (of diamagnetism) est absolutement brusque et correspond exactement avec le phénomène de la fusion · · ·"; and furthermore: "· · · Un curieux phénomène se produit si l'on chauffe le Bi en petits fragments dans une ampoule fermée à une temperature à peine supérieure à celle de fusion. La chute des propriétés magnetiques se produit complètment; cependant si l'on refroidit quelques minutes après, on retrouve les petits fragments qui ont le méme aspect qu'avant et se ne sont pas écroulés. Cependant le Bi. a été fondu, car, en cessant les morceaux, on voit que la structure interne a été complètment changée et que les plans de clivage ne sont plus placés comme avant · · · ·"

This does not mean necessarily an indication of the existence of a transformation, since similar experiments by us showed that even a thin oxide-coat covering such fragments is very well able to preserve their exterior shape, though a pinch with a needle through this (almost invisible) coat proved the interior to be liquid. Furthermore the change of orientation within those fragments makes a melting more probable than an allotropic transformation, since, as is shown by several authors, the main orientation of a crystal is preserved in general no matter how frequently the transition between two allotropic transformations be passed. It appears also clearly in Honda's paper (16) that the rise of diamagnetism is associated with the process of crystallization and a personal discussion of this matter that one of the authors (G.) had with Professor Honda at Sendai leaves no doubt that the utmost care was taken with respect to this question.

[13] F. Zwicky, Proc. Nat. Acad. **16,** 211 (1930).

[14] P. Curie, Journ. de physique **4,** 206 (1895).

[15] A. Goetz and M. F. Hasler, Proc. Nat. Acad. **15,** 646 (1929).

magnetical causes.[11,17] This proves that the anisotropic qualities do not disappear when the macroscopic crystal melts.

Thus one is forced to assume that the distortion of the mosaic structure is the result of two different influences: The orienting influence of the field and the orienting influence of the crystal grown already in an orientation enforced upon it by a seed crystal such as was always used in our experiments. As long as both influences work in the same direction (P_2) there is no distortion, whereas in case they work in different ways a distortion must occur, depending on the orientation (P_1 and P_3), as is indicated by the different signs of the described volume effects. The magnitude of these effects can obviously be ascribed partly to the degree of the distortion. Since the conditions in our experiments were kept as constant as possible the different magnitudes (Bi *A*, *B*, *C*, and *D*) especially of the thermoelectric effects of the same orientation can but indicate different degrees of distortions due to the same cause. This makes it probable that the impurities within the crystal determine the energy necessary for a certain change of the mosaic structure.

With regard to such a relation one has to go back to one consequence of Zwicky's theory of the mosaic crystal which has already been suggested by him implicitly: In case a perfect crystal contains a small amount of impurity, too small to form a homogeneous solid solution of the whole crystal, the strange atoms will accumulate in a region where their presence causes the smallest disturbance of the lattice, i.e. within the II-planes. The chance that a certain part of the foreign atoms present in the liquid will accumulate within the II-planes depends on the expression

$$S = \frac{\alpha}{A} \cdot [E_p - E_r]$$

which by applying the Boltzmann principle gives for the probability the expression:

$$P = \text{const} \cdot e^{-\alpha(E_p - E)/AkT}$$

where E_p and E_r are the respective energy contents of the same crystal first when the foreign atoms are put into the lattice at random and second when they are arranged within the II-planes. A represents the affinity of the strange atoms for the formation of a solid solution in the crystallographic constellation under consideration and α stands for the "perfection" of the crystal, including the conditions of crystallisation, absence of external disturbances, inverse speed of growth, etc. It is apparent that the above will only hold for an amount of foreign atoms smaller than or equal to that amount necessary to fill the II-planes with a mono- or bimolecular layer and only for one kind of atoms at the same time. Under the assumption that S is sufficiently large in our crystals one is led to think that the units of the secondary lattice are surrounded by a more or less dense hull of impurities. It is obvious that atoms

[16] K. Honda, Magnetic properties of matter, Tokyo, p. 131, (1928).

[17] L. Schubnikow and W. J. de Haas, Comm. Phys. Lab. Leiden, Nr. 207 c p. 15 (1930).

of different metals should have different effects due to different A's, i.e., similar atoms should have smaller effects than an equal number of dissimilar ones, the correctness of which conclusion is attested for example by the negligible influence of small amounts of Sb within Bi crystals, (Sb forms the same lattice as Bi with only slightly different dimensions) and also by the surprising effect of traces of Ag and Pb (0.02 percent) as already stated by Bridgman, Goetz and Hasler.

The presence of such dissimilar impurities may greatly change the stability of the secondary lattice and thus make it more sensitive to the influence of a magnetic field applied during the formation of the crystal. The large influences that small impurities have on electric volume-effects within Bi crystals make the assumption of a two-dimensional accumulation of impurities (as in the II-planes) necessary since it is difficult to understand that a homogeneous distribution of minute impurities over the whole crystal can produce such large effects, as have been observed by Kapitza for example in the change of conductivity in strong magnetic fields.[3]

It would be interesting to investigate whether or not the diamagnetic properties of these crystals are affected by impurities and also by their formation within strong magnetic fields. Assuming the correctness of Ehrenfest's hypothesis[18] namely that the large diamagnetic susceptibilities are due to electronic orbits extending around more than one nucleus, a change of the mosaic constellation of a crystal would be expected to affect its magnetic qualities, i.e., one should expect that the large diamagnetic susceptibilities are structure sensitive properties. Experiments of this kind are started and the results seem to point in this direction.

Besides the investigation of the intensity distribution of the x-ray reflections on "normal" and "magnetic" crystals which has already been published[8] briefly, another experiment should be mentioned which could throw light on the nature of the suggested distortion of the mosaic structure: namely an experiment upon the magnetostriction of perfect magnetic and normal crystals, for it is to be expected that this effect must be largely influenced by any systematic change of the secondary structure. Experiments of this kind are planned.

[18] P. Ehrenfest, Physica, 388, (1925); Phys. Zeits. **58,** 719 (1929).

HYPERFINE STRUCTURE IN IONIZED BISMUTH

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Abstract

The hyperfine structure of several lines in the spectra of Bi II and Bi III have been determined. A method which facilitates the analysis of partially resolved line patterns is described. The level separations obtained from the analysis are compared with theoretical formulas showing the inadequacy of the present theory for the interaction of external electrons with nuclear spin.

Experimental

THE twenty-one foot eighty thousand line concave grating mounted in the third basement of the laboratory was used in this work. We have used the grating in Paschen mounting with the slit at fifty degrees from the normal. In the third, fourth and fifth orders, where we have worked, linear dispersions range from 0.47 to 0.87 Angströms per millimeter and the practical resolving power is near two hundred thousand. Although the grating shows faint Rowland ghosts this is no limitation to fine-structure work, since these ghosts always lie far outside the fine-structure pattern. In extreme exposures a faint and diffuse line appears close on the short wave-length side of a sharp line. This false line causes little difficulty, however, since it appears only in over exposure and then at a fixed distance from the parent line. Although no attempt was made at temperature control the temperature of the spectrograph room was so constant that no appreciable broadening appeared after a twenty-four hour exposure.

Since the effect of fields and pressures in broadening spectral lines is considerable for ordinary light sources, special precautions attempting to avoid these influences are necessary in hyperfine structure work. Back has employed his vacuum arc most successfully in his work in arc spectra. Schüler[1] suggests the use of a modified form of the Paschen hollow cathode tube operating at liquid air temperatures. This type of source has been used by White and Ritchl[2] as well as by Schüler himself.

We have used an arc between a bismuth and a tungsten electrode in hydrogen at a few centimeters pressure in making a preliminary survey of the spectrum. This source gave several of the Bi II lines with fair sharpness. Later we used a metal discharge tube similar to that described by Schüler. Our only modification of Schüler's tube is the use of a removable molybdenum cylinder as hollow cathode. This molybdenum cathode has the advantage of contributing practically no lines to the spectrum and of being cleaned of im-

[1] H. Schüler, Zeits. f. Physik **56,** 149 (1930).
[2] H. E. White and R. Ritchl, Phys. Rev. **35,** 1146 (1930).

purities quickly. The bismuth was excited in helium, the metallic bismuth being placed inside the molybdenum cathode. The tube was operated in a water bath since lower temperatures were found to be of no advantage in the case of bismuth. In the discharge the lines of Bi I and Bi II appeared with nearly equal intensity while those of Bi III were somewhat less intense. An exposure of twenty-four hours was necessary in order to obtain some of the lines in the higher orders.

Analysis

The theory concerning hyperfine structure term separations predicts that hyperfine multiplets will follow the interval rule very accurately. Also the formulas for the line intensities in hyperfine line multiplets, which Hill[3] has derived by means of the quantum mechanics, should hold with accuracy. The fact that the interval and intensity rules can be relied upon enables one to construct graphs which aid greatly in the analysis of hyperfine line patterns. An observed line pattern is seldom completely resolved due to small separation in one or the other of the hyperfine multiplets giving rise to the line. The graphs are of particular use in the cases of imperfectly resolved line patterns.

Fig. 1a shows such a graph representing the possible line patterns in the case of a transition between two sets of levels in Bi II, each with a total extra-nuclear angular momentum of one quantum unit ($J=1$). Since the nuclear angular momentum quantum number of bismuth has been shown by Goudsmit and Back[4] to be $4\frac{1}{2}$, the resulting hyperfine multiplets should both be triple with fine quantum numbers of $3\frac{1}{2}$, $4\frac{1}{2}$, and $5\frac{1}{2}$. According to the interval rule the level separations should be $4\frac{1}{2}A$ and $5\frac{1}{2}A$, where A is called the separation factor. The distribution of the lines in the figure at any particular horizontal level gives a possible line pattern. The vertical coordinate, denoted by μ, is the ratio between the separation factors of the initial and final states. If B is the separation factor of the initial and A of the final hyperfine multiplet, $\mu=B/A$. The horizontal coordinate may be read in units of wave length or frequency as one chooses. Thus on the axis, $\mu=0$, we have a line pattern corresponding to the case of no separation of the initial levels, that is, a line triplet with the separations of the final multiplet, the separation ratio being $4\frac{1}{2}:5\frac{1}{2}$ as the interval rule requires. Positions a little above this axis, $\mu=0$, give line patterns due to slight separation of the initial levels as compared with the final levels. As we proceed to larger μ the graph represents the change in line pattern resulting from larger separations of the initial levels. The whole region above the axis (μ positive) gives patterns for cases in which both multiplets are regular or both inverted. Positions below this axis (μ negative) give patterns for cases in which one of the multiplets is inverted with respect to the other. The intensities of the lines are calculated from the formulas of Hill and the widths of the lines made roughly proportional to the expected intensities.

Fig. 1b gives a six-fold enlargement of the line λ5270 of Bi II. It may be

[3] E. L. Hill, Proc. Nat. Acad. Sci. **15**, 779 (1929).

[4] S. Goudsmit and E. Back, Zeits. f. Physik **43**, 321 (1927).

observed that the line fits the graph precisely at $\mu = -0.261$. Because of its small intensity the line in the center of the figure does not appear on the photographic plate. The separations of the two multiplets giving rise to the line may here be read directly from the measured line separations.

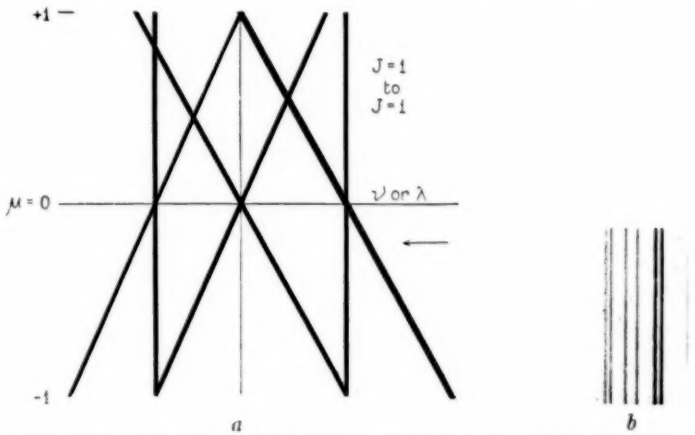

Fig. 1. Diagram for transition $J=1$ to $J=1$ compared with Bi II λ5270. $\mu=-0.261$, total $\Delta\nu=4.93$ cm^{-1}. The arrow indicates where the line pattern fits the diagram.

The graphs are of greatest assistance in cases in which the observed line patterns are imperfectly resolved.[5] In such cases the level separations may be found if μ can be determined by comparing the observed pattern to the graph and one or two separations measured to give the scale. Fig. 2a gives

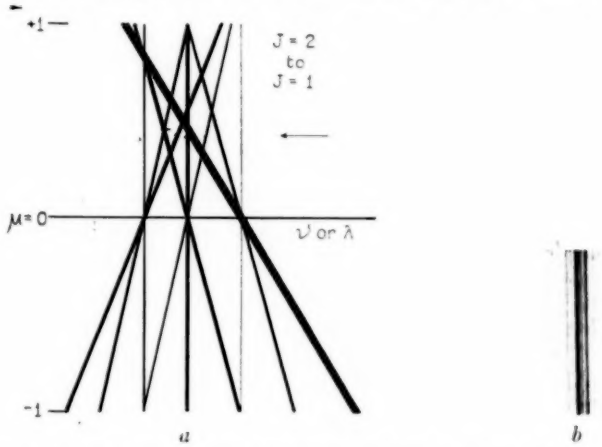

Fig. 2. Diagram for transition $J=2$ to $J=1$ compared with Bi II λ4705. $\mu=+0.457$, total $\Delta\nu=2.71$ cm^{-1}. The arrow indicates where the line pattern fits the diagram.

the graph for the transition $J=2$ to $J=1$. Fig. 2b gives an example of a partially unresolved and poorly defined line pattern which may be analyzed by means of the graph. The pattern is a six-fold enlargement of the unclassified line λ4705 of Bi II as it appeared in the fourth order. It is found that this line

[5] Similar graphs applicable to Zeeman effect analysis are being prepared for publication.

TABLE I. *Hyperfine structure of Bi II lines.*

λ / ν	Intensity of components	$\Delta\nu$ cm^{-1}	Combination
5719	40	3.895 ± .006	$2_1^0-7_2$
17480	50	2.140 ± .006	
	60	.000	
	20	4.926 ± .004	
5270	20	3.995 ± .004	
18970	20	3.166 ± .004	$2_1^0-8_1$
	20	2.149 ± .004	
	23	.553 ± .006	
	25	.000	
	15	3.215 ± .006	
5209	30	2.667 ± .006	
19192	90	2.166 ± .006	
	30	1.471 ± .009	$2_1^0-9_2$
	15	.964 ± .012	
	80	.783 ± .012	
	30	.000	
	8	− .694 ± .009	
	15	1.027 ± .007	
5144	20	.564 ± .007	$1_0^0-8_1$
19435	30	.000	
	5	1.850 ± .006	
5124	7	1.505 ± .009	
19510	10	1.105 ± .009	$9_2^0-16_1$
	14	.585 ± .006	
	18	.000	
	1	2.32 ± .02	
5091	2	1.83 ± .02	
19637	2	1.34 ± .03	$9_2^0-17_1$
	1	1.11 ± .03	
	3	.74 ± .03	
	1	.56 ± .03	
	5	.00	
	20	1.325 ± .007	
4994	5	1.071 ± .007	
20018	10	.734 ± .007	$10_1^0-19_2$
	8	.546 ± .007	
	10	.000	
	4	1.54 ± .03	
4730	10	1.35 ± .02	
21136	12	.99 ± .01	$9_2^0-19_2$
	12	.68 ± .01	
	6	.46 ± .02	
	6	.24 ± .02	
	15	.00	
	2	− .25 ± .02	
	7	2.058 ± .005	
4705	25	1.500 ± .005	
21248	10	1.017 ± .005	Unclassified
	30	.786 ± .003	
	8	.326 ± .008	
	12	.000	
	4	− .652 ± .005	
	3	3.53 ± .02	
4477	3	3.14 ± .02	
22330	3	2.33 ± .03	Unclassified
	3	1.50 ± .02	
	4	.49 ± .02	
	4	.00	

TABLE I (*Continued*)

λ ν	Intensity of Components	Δν cm^{-1}	Combination
	6	.64 ±.02	
4392	6	.30 ±.01	unclassified
22762	3	.00	
	10	2.62 ±.01	
4301	14	2.17 ±.01	
23244	6	1.70 ±.01	$7_2^0-12_3$
	12	1.52 ±.01	
	5	1.03 ±.01	
	18	.81 ±.01	
	5	.295±.005	
	24	.000	
	20	1.52 ±.01	
4079	15	.69 ±.01	
24509	10	.00	$6_1^0-10_2$
	7	1.45 ±.02	
3864	5	.66 ±.03	
25873	3	.00	$6_1^0-15_1$
	1	2.69 ±.04	
3846	2	2.14 ±.03	
25994	3	1.55 ±.02	$5_2^0-10_2$
	4	.88 ±.02	
	5	.00	
	4	3.21 ±.02	
3816	7	2.65 ±.01	
26198	15*	1.96 ±.01	$5_2^0-12_3$
	2	1.23 ±.02	
	10	1.00 ±.01	
	2	.27 ±.01	
	12	.00	
	2	1.65 ±.02	
3811	3	1.31 ±.02	
26232	5	.89 ±.01	$7_2^0-16_3$
	7	.47 ±.01	
	9	.00	
	6	1.25 ±.02	
3792	18	1.07 ±.02	
26364	22	.76 ±.01	$5_2^0-13_3$
	30	.41 ±.01	
	3	.00	
	20	8.84 ±.02	
3430	30	7.30 ±.03	
29146	40	5.29 ±.03	$4_2^0-12_3$
	50	2.88 ±.03	
	60	.00	
	1	8.2	
3111†	2	6.7	
32135	3	4.8	$4_2^0-16_3$
	4	2.7	
	5	.0	
	16	7.5	
2368†	12	5.1	
42217	10	3.0	$4_2-4_2^0$
	9	1.4	
	8	.0	

* An iron line coincides with this component giving the abnormal intensity.
† From the measurements of McLennan, McLay and Crawford.

pattern fits the graph with exactness at $\mu = 0.457$. The very faint component to the extreme right, which may not appear in the reproduction, is present on the original plate.

TABLE II. *Hyperfine structure of Bi III lines.*

λ / ν	Intensity of Components	$\Delta\nu$ cm^{-1}	Combination
	1	9.3 ± .3	
4750	2	8.1 ± .3	
21046	3	6.6 ± .3	$3_{2\frac{1}{2}} - 5f\ ^2F_{2\frac{1}{2}}^0$
	4	4.7 ± .2	
	5	2.6 ± .1	
	6	.0	
	20	2.88 ± .01	
4561	5	2.36 ± .01	
21919	10	.52 ± .01	$7s\ ^2S_{\frac{1}{2}} - 7p\ ^2P_{\frac{1}{2}}^0$
	20	.00	
3695	10	2.16 ± .03	
27056	15	.00	$7s\ ^2S_{\frac{1}{2}} - 7p\ ^2P_{1\frac{1}{2}}^0$
	2	12.3	
3039†	3	10.7	
32896	4	8.9	$2_{2\frac{1}{2}} - 7p\ ^2P_{1\frac{1}{2}}^0$
	5	6.6	
	7	3.6	
	9	.0	
	2	7.1	
2944†	3	5.4	
33957	4	3.0	$1_{1\frac{1}{2}} - 7p\ ^2P_{\frac{1}{2}}^0$
	6	.0	
	1	9.3	
2184†	1	8.0	
45733	1	6.6	$3_{2\frac{1}{2}} - 6f\ ^2F_{3\frac{1}{2}}^0$
	2	4.9	
	2	2.8	
	3	.0	

† From the measurements of McLennan, McLay and Crawford.

Tables I and II give the measurements on the line patterns of Bi II and Bi III, respectively, in terms of frequency differences. The line of the pattern from which the frequency differences are measured is in general the one of lowest frequency. In the few cases in which the line of lowest frequency is faint or unsuitable for other reasons another line has been selected. The method of measurement was such that the uncertainty in frequency difference between any two components of a pattern is not greater than the larger uncertainty following one of them, i.e., the uncertainties do not add. In the tables we give the wave-lengths to four significant figures only, since the patterns are broad and we have not made precise wave-length measurements.

We have been aided greatly in the hyperfine structure analysis by a paper recently published by McLennan, McLay and Crawford[6] in which they give the term analysis for Bi II and for Bi III and a few very wide hyperfine-structure measurements. We have included their measurements in our tables as those indicated by the symbol †.

[6] J. C. McLennan, A. B. McLay and M. F. Crawford, Proc. Roy. Soc. **A129,** 579 (1930).

TABLE III. *Bi II level separations.*

Term value	Configuration*	Term designation	Total separation cm^{-1}	Separation factor
69126	$6p_{\frac{1}{2}}7s$	1_0^0	—	
69590	$6p_{\frac{1}{2}}7s$	2_1^0	3.91 ±0.01	0.391
76143	$6s6p^3$	4_2^0	8.2 ±0.2	0.41
79083	$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}$	5_2^0	2.55 ±0.10	0.127
80569	$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}$	6_1^0	−1.65 ±0.05	−0.165
82041	$6p_{\frac{1}{2}}6d_{2\frac{1}{2}}$	7_2^0	1.98 ±0.15	0.099
88763	$6p_{1\frac{1}{2}}7s$	9_2^0	2.18 ±0.10	0.109
89877	$6p_{1\frac{1}{2}}7s$	10_1^0	−0.53 ±0.03	−0.053
88559	$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}$	8_1	1.02 ±0.01	−0.102
88781	$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}$	9_2	2.50 ±0.03	0.125
105077	$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}$	10_2	−0.16 ±0.06	−0.008
105281	$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}$	12_3	−0.70 ±0.15	−0.023
105443	$6p_{\frac{1}{2}}5f_{3\frac{1}{2}}$	13_3	1.95 ±0.20	0.065
106441	$6p_{1\frac{1}{2}}7p_{\frac{1}{2}}$	15_1	−0.36 ±0.08	−0.036
108272	$6p_{1\frac{1}{2}}7p_{1\frac{1}{2}}$	16_2	0.37 ±0.15	0.012
108398	$6p_{\frac{1}{2}}8p_{\frac{1}{2}}$	17_1	−0.14 ±0.10	−0.014
109897	$6p_{1\frac{1}{2}}7p_{1\frac{1}{2}}$	19_2	0.78 ±0.04	0.039

* The configurations and term values are as given by McLennan, McLay and Crawford.

TABLE IV. *Bi III level separations.*

Term value	Configuration	Term designation	Total separation cm^{-1}	Separation factor
123143	$6s6p^2$	$1_{1\frac{1}{2}}$	7.5 ±0.8	0.50
116943	$6s6p^2$	$2_{2\frac{1}{2}}$	12.5 ±0.8	0.50
111105	$7s$	$^2S_{\frac{1}{2}}$	2.36 ±0.01	0.472
89765	$6s6p^2$	$3_{2\frac{1}{2}}$	9.3 ±0.6	0.37
89188	$7p$	$^2P_{\frac{1}{2}}^0$	0.52 ±0.01	0.104
84053	$7p$	$^2P_{1\frac{1}{2}}^0$	0.31 ±0.05	0.021

Tables III and IV give the level separations as determined from our measured line patterns with the aid of the graphs. In the tables we have used the term designation as given by McLennan, McLay and Crawford. In all cases we give the total hyperfine-multiplet separation. Negative separation in the table indicates inversion of the multiplet. Although the individual level separations could usually be determined, the uncertainty was in most cases too large for the data to be a valuable test of the interval rule. The separations of two of the multiplets of bismuth II are determined with a higher degree of accuracy. They are:

Term	Total separation	Individual separations	
2_1^0	3.91 ± .01	2.15 ± .01	1.76 ± .01
8_1	−1.02 ± .01	− .56 ± .01	− .46 ± .01

We may say that the interval rule is obeyed to within the limit of observational uncertainty in all cases. We believe that the estimates of uncertainty given in the tables are extremely liberal.

It is evident that the hyperfine structure analysis serves to verify much of the term assignment of McLennan, McLay and Crawford from the fact that we are able to use their term designation. We find, however, no evidence of the existence of the tentative term denoted by them as 3°.

We have been able to measure the structure of three lines which without doubt belong to Bi II but which have not been classified by McLennan, McLay and Crawford. We make no attempt to classify these lines in the general term system but do give the hyperfine separations of the levels from which they originate. Two possibilities arise in such cases since there is no way of deciding which level is initial. These lines and the level separations derived from them are as follows:

Wave-length of line	Total separation of initial levels	Total separation of final levels
4705	2.48 ± 0.05 $(J=2)$	2.71 ± 0.01 $(J=1)$
	or	
	-2.71 ± 0.01 $(J=1)$	-2.48 ± 0.05 $(J=2)$
4477	-0.85 ± 0.04 $(J=2)$	2.68 ± 0.04 $(J=2)$
	or	
	-2.68 ± 0.04 $(J=2)$	0.85 ± 0.04 $(J=2)$
4392	0.60 ± 0.15 $(J=1)$	small $(J=0?)$
	or	
	small $(J=0?)$	-0.60 ± 0.15 $(J=1)$

Theoretical Discussion

In a previous[7] paper one of us has given formulas for the hyperfine-structure separations for different states of the same atom. In that paper it was already pointed out that the theoretical results were in disagreement with the experimental data, even in the simple case of a one-electron spectrum. We now wish to discuss our material in Bi II and Bi III together with the known data for Bi I[8] in the light of these theoretical expressions.

Bismuth I. The normal state, $6p^3$, does not yet show extreme (j,j) coupling. We may, however, apply the formulas derived on the assumption of extreme (j,j) coupling to the two levels with $J=2\frac{1}{2}$ and $J=\frac{1}{2}$, respectively, since these two quantum numbers occur only once in this configuration and the hyperfine separations of the levels are therefore independent of the type of coupling. The individual electrons of the configuration are considered as acting separately except for their screening effect upon one another. Thus the separation factor of a hyperfine multiplet is expressible in terms of separation factors for the electronic states. These considerations are similar to those used in the treatment of ordinary multiplet separations. The following table gives the observed separation factors for several states together with the formulas[9] applying both in case of (j,j) coupling and of Russell-Saunders coupling.

[7] S. Goudsmit, Phys. Rev. **37**, 663 (1931).
[8] P. Zeeman, E. Back and S. Goudsmit, Zeits. f. Physik **66**, 1 (1931).
[9] For all following formulas see S. Goudsmit, Phys. Rev. **37**, 663 (1931).

Term	Observed separation factor	Formula	
		(j,j) coupling	Russell-Saunders coupling
$6p^3\ {}^4S_{1\frac{1}{2}}$	~ -0.005	a'	0
$\quad {}^2D_{1\frac{1}{2}}$	-0.040	$1\frac{1}{3}a'-\frac{1}{3}a''$	$^{16}/_{25}a$
$\quad {}^2D_{2\frac{1}{2}}$	0.081	$\frac{2}{3}a'+\frac{1}{3}a''$	$^{24}/_{25}a$
$\quad {}^2P_{\frac{1}{2}}$	0.375	a''	$2\frac{2}{3}a$

In (j,j) coupling the separation factor for the $6p_{1\frac{1}{2}}$ electron is denoted by a' and that for the $6p_{\frac{1}{2}}$ electron by a''. In Russell-Saunders coupling it has no meaning to distinguish between the $6p_{\frac{1}{2}}$ and the $6p_{1\frac{1}{2}}$ states so one can only express the separation factor in terms of the common quantity, a. The quantities a' and a'' are not independent, for, according to the theory, one has the relations,

$$a' = \frac{8}{15}a \text{ and } a'' = \frac{8}{3}a, \text{ thus } a' = \frac{1}{5}a''.$$

The experimental data are not at all in agreement with these results. The last two states in the table, for which the formulas ought to hold, regardless of the type of coupling, show clearly that a' is much smaller than $1/5a''$. One finds from these two levels

$$a' = 0.008$$
$$a'' = 0.375.$$

These values do not agree exactly with those obtained from the first two levels of the table, but this may be ascribed to the deviation from the extreme (j,j) coupling. It is certainly significant that the $^2D_{1\frac{1}{2}}$ level shows a negative separation factor again indicating that a' is too small.

The next configuration of interest is $6p^27s$. The assignment of electron configuration in this case is not quite certain as this configuration is mixed with the $6p^26d$ levels. This also may cause large second order corrections which make our formulas invalid. The observed data for this configuration, which is near extreme (j,j) coupling, together with the formulas applying in (j,j) coupling are as follows:

Term	Observed separation factor	Formula (j,j) coupling
$6p^27s\ 1_{\frac{1}{2}}$	0.166	c
$\quad 4_{1\frac{1}{2}}$	~ 0	$\frac{5}{6}a'-\frac{1}{6}a''+\frac{1}{2}c$
$\quad 5_{\frac{1}{2}}$	-0.142	$1\frac{2}{3}a'-\frac{1}{3}a''-\frac{1}{2}c$
$\quad 7_{2\frac{1}{2}}$	0.127	$\frac{2}{3}a'+\frac{1}{3}a''+\frac{1}{2}c$
$\quad 8_{1\frac{1}{2}}$	0.094	$^9/_{10}a'+^3/_{10}a''-\frac{1}{2}c$

Here the separation factor of the $7s$ electron is denoted by c. In this example the first level lies isolated from the others, hence one expects the formula to hold. The other levels form a group in which levels with $J=\frac{1}{2}$ and $J=2\frac{1}{2}$ occur only once. For these two levels the formulas ought also to be correct. From these one obtains:

$$c = 0.166$$
$$a' = 0.026$$
$$a'' = 0.390.$$

These values are in fair agreement with the data for the two observed levels with $J = 1\frac{1}{2}$. The value of a'' is in good agreement with what we obtain from the p^3 configuration. The value of a' agrees only in order of magnitude. However, we may not rely too much upon this value since it is so small that it may be much influenced by inaccuracy in the data as well as by second order corrections to our formulas. The significant point is that we again find a' to be much smaller than $1/5a''$.

Bismuth II. For the configuration $6p\ 7s$ we have extreme (j,j) coupling. The formulas and observed data for this case are:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}7s\ 2_1^0$	0.391	$\frac{1}{2}a''+\frac{1}{2}c$
$6p_{1\frac{1}{2}}7s\ 9_2^0$	0.109	$\frac{3}{4}a'+\frac{1}{4}c$
10_1^0	−0.053	$1\frac{1}{4}a'-\frac{1}{4}c$

We expect the values of a', a'' and c to be somewhat larger than in Bi I because the screening has decreased. This will have the greatest influence upon the outer $7s$ electron and therefore upon c. We find

$$a' = 0.028$$
$$a'' = 0.430$$
$$c = 0.352$$

These values are in good agreement with our expectation.

For other configurations, such as $6p\ 6d$ and $6p\ 7p$, we expect only qualitative agreement, as the separation factors for the $6d$ and $7p$ are probably smaller than the errors due to second order corrections to our formulas and errors in our measurements. In the case of the $6p\ 6d$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}\ 5_2^0$	0.127	$\frac{1}{4}a''+\frac{3}{4}d''$
6_1^0	−0.165	$-\frac{1}{4}a''+1\frac{1}{4}a''$
$6p_{\frac{1}{2}}6d_{2\frac{1}{2}}\ 7_2^0$	0.099	$-\frac{1}{6}a''+1\frac{1}{6}d'$

Here the symbols d' and d'' denote the separation factors of the $6d_{2\frac{1}{2}}$ and $6d_{1\frac{1}{2}}$ electrons, respectively. The first two states give:

$$a'' = 0.565$$
$$d'' = -0.019$$

It is strange to find a small negative value for d'', but we do not know that this value is entirely reliable. The experiment result for 7_2° would give a very large value for d', which is even less understandable. Perhaps the assignment of the configuration is incorrect for this level.

As examples of the $6p\ 7p$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}\ 8_1$	−0.101	$-\frac{1}{4}a''+1\frac{1}{4}e'$
9_2	0.125	$\frac{1}{4}a''+\frac{3}{4}e'$

Here e' denotes the separation factor for the $7p_{1\frac{1}{2}}$ state. We find:

$$e' = 0.012$$
$$a'' = 0.464.$$

Again a'' is in good agreement with what we expect.

For the $6p\ 5f$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}\ 10_2$	−0.008	$-\frac{1}{6}a''+1\frac{1}{6}f''$
12_3	−0.023	$\frac{1}{6}a''+\frac{5}{6}f''$
$6p_{\frac{1}{2}}5f_{3\frac{1}{2}}\ 13_3$	0.065	$-\frac{1}{6}a''+1\frac{1}{6}f'$

Here f'' denotes the separation factor of the $5f_{2\frac{1}{2}}$ electron and f' that of the $5f_{3\frac{1}{2}}$ electron. These data give no sensible result. Perhaps the assignment of configuration is incorrect, or it may be that there are large second order effects due to the proximity of these levels to other even levels.

Bismuth III. The interesting configuration here is $6s\ 6p^2$. The hyperfine structure is known for three of the levels. For extreme (j,j) coupling, which may not be quite correct here, we have:

Term	Observed separation factor	Formula (j,j) coupling
$6s\ 6p^2\ 1_{1\frac{1}{2}}$	0.50	$\frac{3}{5}a'-\frac{1}{6}a''+\frac{1}{3}b$
$2_{2\frac{1}{2}}$	0.50	$\frac{3}{5}a'+\frac{1}{6}a''+\frac{1}{3}b$
$3_{2\frac{1}{2}}$	0.37	$\frac{1}{5}a'+\frac{1}{3}b$

The separation factor of the $6s$ electron is here denoted by b. The above data give us:

$$a'' = 0.66$$
$$a' = 0.01$$
$$b = 1.80.$$

Due to the fact that the screening is here much less than in the previous cases we find a'' to be larger than before. We cannot, of course, be sure that the value found is just the one expected without making complicated calculations as to screening effects. The value of a' is smaller than the uncertainty in measurement and therefore not reliable.

For the $7s$ configuration we find:

Term	Observed separation factor	Formula (j,j) coupling)
$7s\ ^2S_{\frac{1}{2}}$	0.472	c

Comparing this value of c with the previous values we find the expected large increase. The experimental values for c are, Bi I:0.166; Bi II:0.352; Bi III:0.472.

We can make a similar comparison of the separations due to the 6*s* electron. The large hyperfine structure of the far ultraviolet lines λ864 and λ1139 observed by Arvidson[10] is probably that of the 6*s* state of Bi V. Furthermore, one level of the $6s\,6p^3$ configuration of Bi II is at present known. Assuming (j,j) coupling one obtains:

Term	Observed separation factor	Formula (j,j) coupling
Bi II $6s6p^3\ 4_2^0$	0.41	$\frac{3}{4}a'+\frac{1}{4}b$
Bi V $6s$	2.6	b

Since a' is of the order of 0.01 this gives $b=1.60$ for Bi II. Comparing the different values for b, we find, Bi II: 1.60; Bi III: 1.80; Bi V: 2.6.

Conclusions

The above discussion shows that in some respects the experimental results obey the theoretical formulas whereas in others there is distinct disagreement. It is possible to determine in more detail where the discrepancy lies. The formulas as they are given here in terms of a' and a'' explicitly are more or less independent of the type of interaction which causes the hyperfine splitting. One takes a given interaction for a definite state of a single electron and calculates by means of well-known methods the result when this electron is not alone but part of a more complicated configuration. Such formulas are based upon well-known quantum mechanical rules and can in many cases be derived by simple methods using the vector model. Similar ones have been shown to hold for multiplet separations, *g*-values, etc. It is therefore not surprising that the formulas are also valid here, for if they were not it would mean that ordinary perturbation theory could not be applied to our problem.

The discrepancy was found, however, in the relation between a' and a'',

$$a' = \frac{1}{5}\,a''.$$

Everywhere we find a' much too small. This relation, however, can be obtained only by considering in detail the interaction between the nuclear spin and the orbital and spin magnetism of the external electrons.[11] It is on this point that the present theory seems to be incorrect. We hope that the material gathered here may prove useful as a guide for the improvement of the quantum mechanics of spin-spin interaction.

[10] G. Arvidson, Nature **126,** 565 (1930).

[11] Compare S. Goudsmit, Phys. Rev. **37,** 663 (1931).

POTENTIAL DROP AND IONIZATION AT MERCURY ARC CATHODE

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(Received March 19, 1931)

Abstract

By means of a movable Langmuir collector, the potential, ion concentration and electron temperature were measured at various distances from a stationary mercury cathode spot, at various arc currents. The results indicated a cathode drop of 10.0 volts, and a small negative potential gradient beyond the fall space which was more pronounced at the larger currents. The ion concentration varied between $2(10)^{13}$ and $3(10)^{11}$ cm^{-3} for distances between 0.4 cm and 1.7 cm and arc currents between 11 amp and 4.2 amp. The concentrations evidently greatly exceed these values very close to the cathode. The mean electron energies were about 1.4 volts near the cathode and fell to a little less than a volt at the greater distances. From the lack of saturation of currents to the collector at space potential, the coefficient of electron reflection at the amalgamated tungsten collector surface was found to be close to 0.5. It is shown that the thickness of the cathode fall space must be less than $1.76(10)^{-4}$ cm and that the field at the cathode surface must exceed $7.6(10)^{4}$ volts $\cdot$ cm^{-1}.

Introduction

In 1905, Stark and his collaborators[1] attempted by a probe wire method to measure the cathode fall of potential in a mercury arc, and their value of 5.27 volts has been accepted until quite recently. In 1924, Langmuir and Mott-Smith[2] pointed out a serious error in the old probe wire method, and developed a new method which not only gives accurate values of space potential, but also gives information regarding electron and ion concentrations and velocities. In 1928, Killian, at the suggestion of one of the authors, undertook an investigation of the potential drop and conditions of ionization near mercury arc cathodes. His results were reported at a meeting of the American Physical Society[3] and were essentially as follows: The drop in potential from the cathode to a point distant 0.2 cm from its surface was 10.1 volts, and increased regularly to 11.6 volts as the distance was increased to 3.0 cm. The value of about 10 volts, as extrapolated to the cathode surface has been taken as significant of the ionizing potential of mercury within the limits of uncertainty set by the small unknown contact difference of potential between cathode and probe.[4] Later work by Nottingham[5] has led to similar conclusions

[1] Stark, Retschinsky and Shaposchnikoff, Ann. d. Physik **18,** 213 (1905).

[2] Langmuir and Mott-Smith, G. E. Rev. **27,** 449, 538, 616, 762, 810 (1924).

[3] Killian, Phys. Rev. **31,** 1122 (1928).

[4] Gaudenzi (The Brown Boveri Rev. **16,** 303 (1929)) estimated the cathode drop to be about 9 volts by a method which did not allow for the possibility of a positive or negative anode drop.

[5] Nottingham, J. Frank. Inst. **206,** 43 (1928); **207,** 299 (1929).

in some arcs at higher pressures with various cathode materials. Killian furthermore found random currents of positive ions of 1.5 to 40 milliamps·cm^{-2} and of electrons of 1.3 to 18 amps·cm^{-2}, the larger values referring to the regions closest to the cathode. The electron temperatures were 5000° to 16,500°K, or 0.65 to 2.13 volts mean energy.

In these measurements, the distances were measured from the cathode surface but do not represent true distances from the cathode spot, since it wandered rapidly and erratically all over the cathode surface. Killian there-

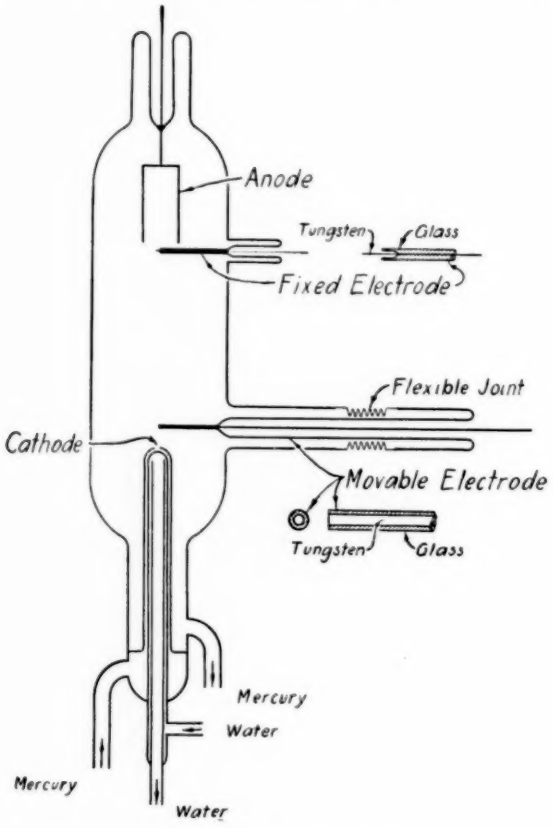

Fig. 1. Diagram of arc tube.

fore devised the apparatus described below in order to keep the cathode spot approximately stationary and thus to make possible more accurate measurements. Since Killian was diverted from carrying out these more refined experiments, the authors continued them as follows.

Apparatus

A diagram of the arc tube is shown in Fig. 1. The cathode consists of three coaxial tubes. The innermost two are of Pyrex glass and constitute a water-cooling system for the cathode. The outside tube is of quartz and has a small hole drilled in its upper end. Mercury is raised to the level of this hole.

The surface of the mercury at the hole is the cathode of the arc. The small size of the pool cathode thus prevents excessive wandering of the cathode spot. The mercury outlet shown is designed to take care of the mercury that condenses on the walls of the tube and falls to the bottom.

The exploring electrode employed in the region of the cathode consists of a 60 mil tungsten wire entirely covered with glass, and then ground flat at its end. The resulting flat tungsten surface constitutes a plane collector, and the great mass of tungsten behind it makes its thermal dissipating power sufficiently great to prevent the excessive heating which has hitherto made measurements very near the cathode spot impossible. The flexible metal joint shown in the diagram permits an exploring range of about 2 cm.

The exploring wire shown near the anode is of the usual type consisting of a fine tungsten wire covered with glass over most of its length. The last few millimeters of glass are not in contact with the exploring wire. This prevents electrical contact between the exploring wire and any metal coating which may be deposited on the insulating glass.

The anode as shown is of the usual hollow cylindrical design and is made of sheet nickel.

Procedure

The arc was started by means of a high frequency leak tester and the current was adjusted to the desired value by varying the resistance in series. The arc and series resistance were operated on 110 volts d.c.

The experimental procedure, after the arc had become steady, was to measure the current to the collector for different voltages applied to it at various distances from the cathode. At any given position, a plot of log i vs. V where i is the electron current to the collector and V the potential of the collector with respect to the cathode generally showed the points to be scattered between two parallel lines a half volt apart. This scattering of the points was found to arise from changes in the nature of the surface of the collector which resulted in changes in the contact difference in potential and depended on the immediately previous history of the collector. It was found that consistent results were obtained if the collector was left 100 volts negative with respect to the anode except when a reading was actually being made. Under these conditions the points fell along a curve at the lower voltage limit mentioned above, indicating a low value for the work function of the surface.

The curves shown are plotted to this lower value, which is believed to be the correct value, for reasons indicated below. Since the collector is always covered with a thin visible film of mercury, there is no further correction necessary for contact difference of potential between collector and mercury cathode.

A typical collector curve is shown in Fig. 2.

Interpretation of Shift in Collector Potential

We were at first inclined to attribute the shift in collector potential, when its potential to space was changed from large negative values to small negative or positive values, to a slow deposit of alkali material coming perhaps

from the neighboring glass and depositing as ions when the collector is negative. In this case the upper curve (characteristic of the collector in its more electronegative state) would presumably be that characteristic of an uncontaminated surface and, if so, the correct values would be 0.5 volt higher than those of Fig. 2. This was our opinion at the time of our preliminary report to the American Physical Society (Washington Meeting April 24, 1930), when we reported as our best estimate that the cathode drop is equal to the minimum ionizing potential 10.4 volts. Now, however, we are inclined to interpret the results differently, and to use the lower value of potential for the following reasons.

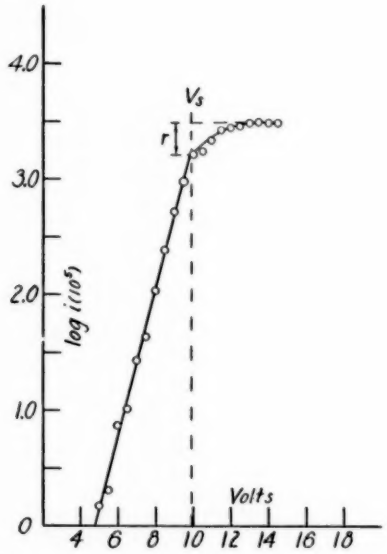

Fig. 2. Curve showing logarithm of electron current i as a function of collector potential V_c with respect to cathode. V_s is space potential and r indicates the amount of electron reflection.

After remaining 100 volts negative for a short time, surface impurities should be sputtered off by positive ion bombardment, leaving a clean collector surface. Hence the measurements made just after this should be those characteristic of the clean surface. Furthermore Found and Langmuir (unpublished) in extending earlier work by Kenty and Turner,[6] found that oxygen layers could form slowly on tungsten collectors even in very pure gas, causing electronegative potential shifts of about 0.5 volts in the surface potential. We think it probable, therefore, that the lower voltage values are the correct ones, indicating the value of the cathode drop to be about 9.9 volts.

Interpretation of Experimental Results

These and similar curves are interpreted by the collector theory of Langmuir and Mott-Smith, which is now too well known to require comment further than to give the equations which we shall use:

[6] Kenty and Turner, Phys. Rev. **32**, 799 (1928).

$$I = I_0 \epsilon^{-eV_c/kT}, \quad I_0 = Ne\left(\frac{kT}{2\pi m}\right)^{1/2}, \quad i = AI$$

where I is the electron current density to the collector whose potential is $-V_c$ with respect to the space, I_o is the random electron current density, N and T are the electron concentration and temperature, respectively, and A is the collector area. From these equations we have:

$$\log i = \log AI_0 - \frac{eV_c}{kT} = \log ANe\left(\frac{kT}{2\pi m}\right)^{1/2} - \frac{eV_c}{kT}$$

which is the equation of the straight portion of the curve of Fig. 2, when V_c is taken to be the value of V measured from the point of discontinuity which is at space potential V_s. The fact that the curve to the left of the discontinuity is straight, proves that the electrons have a Maxwellian distribution of velocities, which is assumed in the above equations.

It is observed that the electron current to the collector does not reach its maximum value at space potential, but only when the collector is a few volts positive with respect to space. This is attributed to electron reflection from the collector, and the intervening curve depends on the distribution of velocities of the reflected electrons. Such reflection, which is a well-recognized phenomenon, does not affect the slope of the straight line to the left of the break, since it is a peculiarity of a Maxwell distribution that it is not altered by a retarding field and hence the fraction of electrons reflected is constant at all values of the retarding field. The effect of reflection on the straight portion of the curve is thus simply to depress it, parallel to itself, by an amount dependent on the reflection coefficient.

This reflection coefficient may be obtained from Fig. 2 as follows. The electron current has reached saturation at about 4 volts above space potential, indicating that practically no reflected electrons can escape against as much as 4 volts. The difference between this saturation current and the current at the discontinuity represents the current of reflected electrons, and is shown by r in Fig. 2. The ratio of this reflected current to the total saturation current gives the reflection coefficient R. Owing to the foreshortening of the logarithmic scale, these values of R are determined with less experimental accuracy than the other quantities in which we are interested.

The more important results of the measurements are shown in Figs. 3 and 4. The mean electron energy $\bar{V}$ was calculated from the relation

$$\frac{e\bar{V}}{300} = \frac{3}{2}kT$$

and represents the mean energy of the electrons in a given volume. For the mean energy of the electrons striking the collector, the fraction 3/2 should be replaced by 2.

The data shown in Figs. 3 and 4 were all obtained with an arc carrying 4.2 amps. Similar observations on an 11.0 amp. arc yielded results which, for comparison, are shown in Table I.

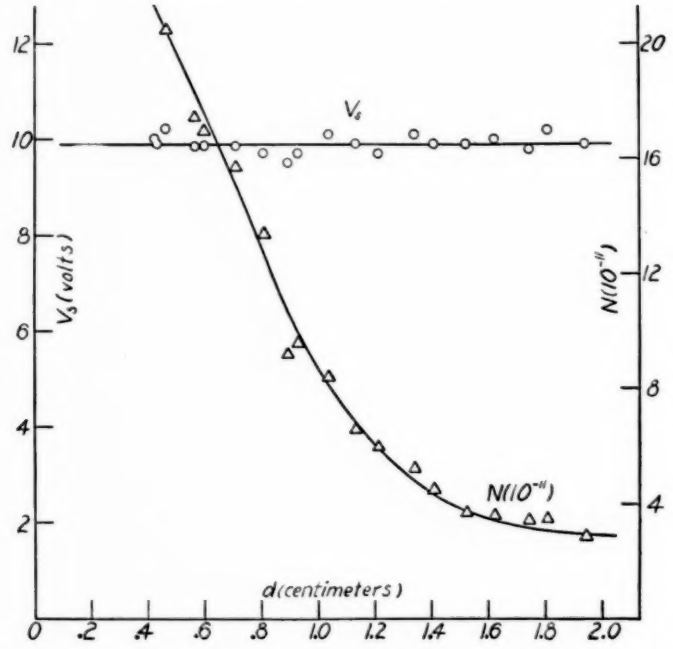

Fig. 3. Space potential V_s with respect to the cathode and electron concentration N as functions of the distance d from the cathode spot to the center of the face of the 60 mil (0.15 cm) diameter collector. Arc current 4.2 amp.

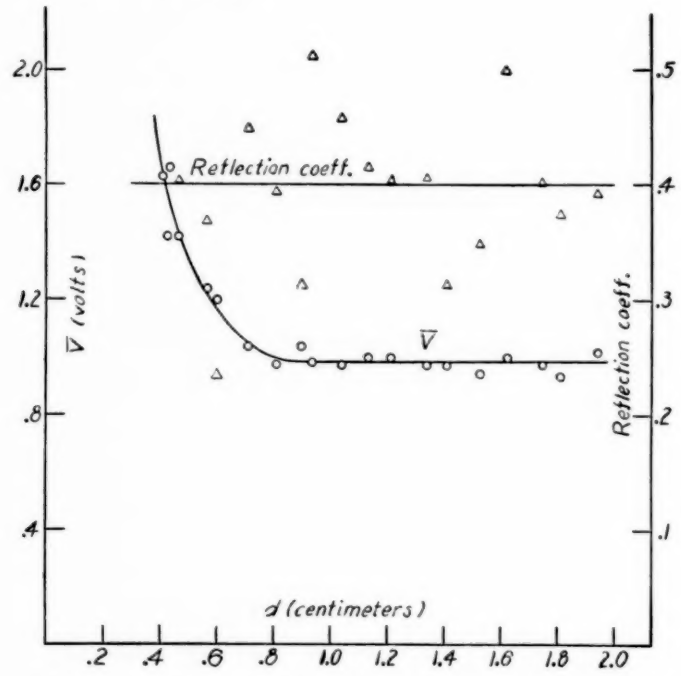

Fig. 4. Mean electron energy $\bar{V}$ in equivalent volts and reflection coefficient R as functions of distance d from cathode spot to collector. Arc current 4.2 amp.

TABLE I. *V_s = space potential; N = electron concentration; $\overline{V}$ = mean electron energy; I = random electron current density; d = distance from cathode.*

	4.2 amp. arc		11.0 amp. arc	
d(cm)	0.43	1.75	0.39	1.71
V_s (volts)	10.0	9.8	10.2	8.9
I (amp·cm^{-2})	5.7	7.4	63.5	12.8
N (10^{-11})	17.1	2.8	218.	55.3
$\overline{V}$ (volts)	1.42	0.978	1.171	0.748

DISCUSSION OF EXPERIMENTAL RESULTS

Cathode drop. From such results we conclude that the cathode drop is very near to 10 volts, from the nearest point at which we can measure (or extrapolate) to the cathode. Of course what we really wish to know is the cathode drop across the cathode fall space alone, which is an extremely small distance. This distance has never been measured, but may be estimated roughly as follows: The relations in the cathode fall space are given by the space-charge equation

$$I_+ = 0.543(10)^{-7}\frac{V_c^{3/2}}{M^{1/2}d_c^2}$$

in ordinary electrical units. The current density at the cathode[7] is about 4000 amp.·cm^{-2}. Langmuir and Mott Smith[8] have shown that a negative electrode immersed in strongly ionized mercury vapor collects a positive ion current of about 1/400 of the "random" electron current, which in turn is always larger than the "drift" (or actual discharge) current. Since the drift current density is 4000 amp.·cm^{-2}, the positive current density is therefore something greater than 1/400 of this, i.e., greater than 10 amp.·cm^{-2}. Unfortunately we cannot say how much greater than this lower limit is the true value of the positive current. Two factors may increase it by considerably more than the factor of three or four which commonly represents the ratio of random to drift current in regions of uniform ionization. One of these is the enormous concentration of electrons and ions in the region of negative glow on account of the potential maximum which develops in this region of intense ionization, and the consequent "trapping" of electrons to build up large concentrations, and the other is the additional trapping action due to the fact that the cathode spot is a depression in the mercury surface and presents therefore the peculiarities of a hollow cathode.

Perhaps the positive ion currents may be ten, though probably not a hundred times the value given by the fraction 1/400.[9] Using this as a lower limit, and taking $V_c = 10$ volts and $M = 200$, we find

$$d_c < 1.76(10)^{-4}\text{ cm}.$$

[7] Güntherschulze, Zeits. f. Physik **11,** 74 (1922).

[8] Langmuir and Mott-Smith, G.E. Rev. **27,** 544 (1924).

[9] From the theory of collectors in ionized gas (Tonks and Langmuir, Phys. Rev. **34,** 876 (1930)) it is impossible that the positive current density at the cathode spot can be less than

Field at cathode. Given a cathode drop of 10 volts in a distance less than $1.76(10)^{-4}$cm, we calculate the average field in the fall space to be greater than $5.7\ (10)^4$ volts·cm^{-1}. By the simple space-charge equation it is easily shown that the field E_c at the cathode surface is 4/3 the mean field, or

$$E_c > 7.6(10)^4 \text{ volts}\cdot\text{cm}^{-1}.$$

It appears unlikely that the field can be as much as ten times this value, since this would require an ion current one hundred fold that on which the calculation is based. These results are not appreciably affected if we use the more refined equations of Mackeown[10] to calculate the value of d_c.

Of course the cathode surface is highly agitated and consequently rough. Thus the fields to points may greatly exceed the values calculated above, and may very likely attain values of the order of millions of volts per centimeter. Langmuir[11] has already pointed out that fields of this magnitude are probably adequate to account for the observed electron emission from the cathode spot as "autoelectronic" emission, or "field current".

In the absence of information regarding the behavior of a fresh mercury surface in autoelectronic emission and in view of the uncertainty regarding the field strength at the cathode, it appears hopeless to make a direct quantitative test of this theory of emission from the cathode spot. Further evidence, however, is afforded in a revision of earlier studies of heat balance, as given in the following paper.

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this. According to one theory it might be much greater (the theory of thermal ionization of the vapor by Slepian, Phys. Rev. **27,** 407 (1926)). As shown in the following paper, however, there are not only serious theoretical objections to this theory, but the experimental evidence based on heat balance at the cathode is inconsistent with it, and points to the correctness of the assumption that the relative current densities are at least of the order of those to be expected if the cathode acts toward the positive ions simply as a collecting electrode.

[10] Mackeown, Phys. Rev. **34,** 611 (1929).

[11] Langmuir, G. E. Rev. **26,** 735 (1923).

ON THE THEORY OF THE MERCURY ARC

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Abstract

The theory of *heat balance at the cathode* is extended (1) by the introduction of the accommodation coefficient of neutralized ions, (2) by evaluation of all processes which absorb the energy gained by electrons in the cathode fall space, and (3) by correction of a previous assumption that fields sufficient to extract electrons will affect the heat of neutralization of postive ions at the surface. Test of the two resulting equations by existing experimental data shows that *Langmuir's theory* of extraction of electrons by the field at a Hg arc cathode is consistent with the cathode heat equations, but cannot be uniquely proved by them on account of uncertainty in two factors whose order of magnitude only is known: the fraction F of energy brought to the cathode by unelectrified carriers, $1.0>F>0.5$; the fraction $1/(1+\delta)$ of positive ions formed near the cathode which go to it, $1>\delta>0$.

From the net rate of evaporation an equation is obtained between vapor pressure and temperature at the cathode which, when combined with the vapor pressure-temperature equation of Hg, gives uniquely the *temperature of the cathode spot* and the *vapor pressure* outside it, provided the fraction f of total current carried by electrons is known. It is shown that the temperature of the cathode spot does not exceed 200°C, and that *the thickness of the cathode fall space is less than the electron mean free path.*

It is shown that *ionization* just beyond the cathode fall space must be of the *cumulative, multiple stage type.* From this it is shown that the fraction f must exceed 0.67 (if $\delta=0$) or 0.80 (if $\delta=1$), since these minimum values depend on 100 per cent efficiency of two stage ionization.

Mechanical pressure against the cathode by the arc is explained by the fact that the accommodation coefficient a is less than 1.0. If this accommodation coefficient of Hg ions at a liquid Hg surface should be independently measured, it would give an independent method of estimating the important fraction f.

The paper points out the causes of present limitations in our knowledge of conditions at the arc cathode and also the manner in which, and the extent to which, these limitations may be removed.

Introduction

THE early theory of Stark[1] that the current at mercury arc cathodes is of thermionic origin has been pretty thoroughly disproved by the fact that the evaporation of mercury is far too slow to justify an assumption of temperatures requisite for thermionic emission. Similarly a theory of Slepian[2] that the current at the cathode is carried by positive ions created by thermal ionization of the vapor just outside the cathode fails to suggest any physical mechanism for the input of energy into this assumed high temperature region. The theory at present in vogue is that of Langmuir,[3] who postulates "field currents" caused by the strong field which is concentrated at the

[1] Stark, Ann. d. Physik **12,** 692 (1903).
[2] Slepian, Phys. Rev. **27,** 407 (1926).
[3] Langmuir, Science **58,** 290 (1923); G. E. Rev. **26,** 735 (1923).

cathode by the processes described by Poisson's equation, and whose minimum value was calculated in the preceding paper to be at least 7.6 $(10)^4$ volts $\cdot$ cm^{-1}.

A difficulty in any theory depending primarily on electron emission from the cathode has been found in attempting to calculate from the heat balance at the cathode the fraction of the current carried by electrons, since such attempts have led consistently to values of this fraction which are too small to reconcile with the necessary amount of ionization, in view of the small cathode drop. For example, substituting direct experimental values of observable quantities in the heat balance equation has led to the conclusion that about 50 per cent of the current at the cathode is carried by electrons. Certain reasonable modifications have raised this to about 70 percent. By straining every possible factor, this proportion has been raised to about 87 percent. These values are all too small to reconcile with the fact that the cathode drop is only about 10 volts (see the preceding paper by Lamar and Compton); for 50 percent current carried by electrons would require 100 percent efficiency of ionization by them in order to obtain an equal number of positive ions to carry the remaining half of the current at the cathode. Even 87 percent would require at least 12 percent efficiency of ionization, which is still far in excess of any observed efficiencies of ionization by impact of electrons whose energy is near the minimum ionizing energy 10.4 volts.

The present paper presents some new considerations of heat balance which make it compatible with Langmuir's theory, and at the same time lead to a much more definite picture of the physical conditions in the mercury arc than has previously been possible.

It may be remarked, in passing, that the entire problem of the mercury arc is concentrated at the cathode, since the work of Langmuir and Mott-Smith,[4] Tonks and Langmuir,[5] Eckart and Compton,[6] and Killian[7] have essentially explained all other regions of a low pressure arc.

Heat Balance at Cathode

The two earliest attempts to use heat balance to investigate cathode conditions were quite unsatisfactory, the one[8] because of faulty reasoning and the other[9] because of lack of essential experimental data. Later refinements[10] have been made both in the theory and the experiments. It will be seen in the following paragraphs, however, that there are so many factors which have not previously been considered that no validity attaches to any of the conclusions thus far drawn from arguments based on heat balance.

[4] Langmuir and Mott-Smith, G. E. Rev. **27,** 449, 538, 616, 762, 810 (1924).
[5] Tonks and Langmuir, Phys. Rev. **34,** 876 (1929).
[6] Eckart and Compton, Phys. Rev. **24,** 97 (1924).
[7] Killian, Phys. Rev. **35,** 1238 (1930).
[8] Güntherschulze, Zeits. f. Physik **11,** 74 (1922).
[9] Compton, Phys. Rev. **21,** 266 (1923).
[10] Güntherschulze, Zeits. f. Physik **31,** 509 (1925); Seeliger, Phys. Zeits. **27,** 22 (1927); Elektrotech. Zeits. **49,** 853 (1927); Compton and Van Voorhis, Proc. Nat. Acad. Sci. **13,** 336 (1927); Issendorff, Phys. Zeits. **29,** 857 (1928).

We shall express the condition of thermal equilibrium by setting the total net rate of generation of heat at the cathode equal to zero, expressing each contributing item of heating or cooling in terms of watts per ampere of current. We shall let f equal the fraction of current carried at the cathode by electrons, and $(1-f)$ the fraction carried by positive ions. The processes involved in the heat balance are schematically indicated in Fig. 1 and will be discussed briefly in order.

(1) *Heating by impacting positive ions.* These ions acquire energy V_c in falling through the cathode potential drop V_c. Since the thickness of the fall space is certainly less than $1.76\ (10)^{-4}$ cm and since, as we shall see below, the ionic mean free path is considerably greater than this, we are justified in neglecting collisions of ions with vapor molecules while passing through this

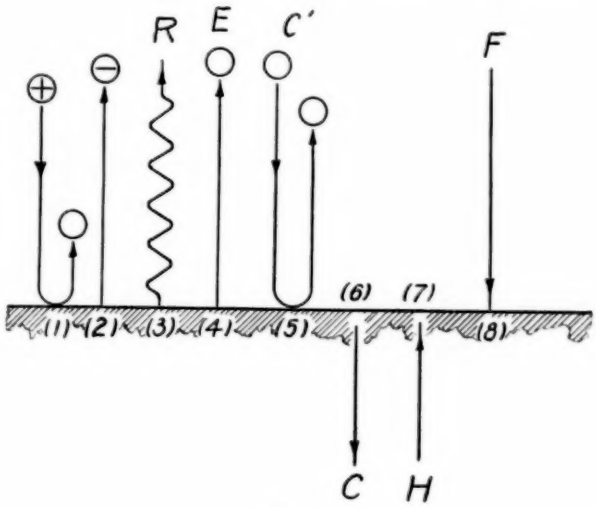

Fig. 1.

fall space. Thus the entire energy V_c is available for delivery to the cathode. To this should be added the average initial kinetic energy of the ions just before they enter the fall space. Tonks and Langmuir[4] have shown that this is negligibly small.

It is not obvious, however, that all this kinetic energy is delivered to the cathode. Let a be the fraction of it which is thus delivered, while $(1-a)$ is the average fraction which is retained by the neutralized ion after impact. This quantity a is the "accommodation coefficient" which is well known in phenomena involving the impact of gas molecules against a surface of different temperature[11] and whose existence in cases of ionic impact has been demonstrated by Van Voorhis and Compton.[12]

[11] Knudsen, Ann. d. Physik **34,** 593 (1911); **46,** 641 (1915); Langmuir, J. Am. Chem. Soc. **37,** 425 (1915); Compton and Langmuir, Rev. Mod. Phys. **2,** 184 (1930).

[12] Van Voorhis and Compton, Phys. Rev. **35,** 1438 (1930); detailed paper in preparation for physical Review.

Finally, there is the "heat of neutralization" of the positive ion, denoted by ϕ_+, whose value has been shown by an argument involving a simple cycle[13] to be $\phi_+ = V_i - \phi_- + (L)$, where V_i is the ionizing potential of the gas molecule, ϕ_- is the electron work function of the cathode surface, and L is the heat of condensation of the neutral molecule on the cathode surface. L should be used if the ion is actually condensed on the surface, but should otherwise be omitted. In our present problem L is completely taken care of in process (4) (Fig. 1).

In case the field appreciably reduces the work function (as in Langmuir's theory it reduces it to zero) it has previously been assumed that the reduced value should be used in this equation, i.e., that if the field changes the cooling effect of electron emission it will also affect the heating effect of positive ion neutralization. This is, however, not the case, as is easily shown by the following argument.

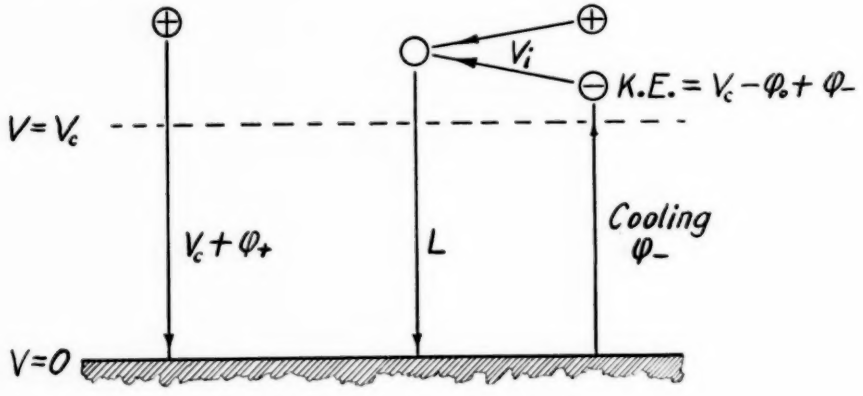

Fig. 2.

A positive ion, starting outside the cathode fall space and moving to the cathode delivers energy $V_c + \phi_+$, as indicated to the left in Fig. 2. An equivalent process is shown to the right. An electron escapes from the metal, cooling it by the amount ϕ_-. By the time it has passed through the fall space its kinetic energy is $V_c - \phi_0 + \phi_-$, where ϕ_- is the "effective" work function while ϕ_0 is the normal work function in the absence of an accelerating field. This is obvious since $(\phi_0 - \phi_-)$ is that part of the work done against the surface forces of the metal which is done by the applied field and ϕ_- is that part done at the expense of initial kinetic energy of the electron. If emission is purely thermionic, then $\phi_- = \phi_0$, whereas if emission is purely autoelectronic (as in Langmuir's theory) then $\phi_- = 0$.

Now if this electron combines with a positive ion, there is liberated additional energy V_i, and there is a further liberation of amount L when the neutralized particle condenses on the metal.

[13] Compton, Phys. Rev. **21**, 281 (1923); Schottky and Issendorff, Zeits. f. Physik **26**, 85 (1924).

Equating the net liberation of energy in the two equivalent processes gives $V_c+\phi_+=V_i+V_c-\phi_0+\phi_--\phi_-+L$, whence

$$\phi_+ = V_i - \phi_0 + L.$$

Thus the heating effect by positive ions is unaffected by the field, even though the cooling effect by escaping electrons is diminished. Physically this is easily explicable, since the cooling effect is due to the fact that only those electrons escape which, while inside the metal, possess greatest kinetic energy, a situation which has no counterpart in the process of neutralizing a positive ion.

In this equation $\phi_+=V_i-\phi_0+(L)$, it is implicitly assumed that all the energy developed by the process is retained in the cathode, which would not be the case, for example, if a fraction $(1-r)$ of it were radiated away in the process of neutralization. Compton and Van Voorhis therefore suggested[14] the modification $\phi_+=rV_i-\phi_0+(L)$, and announced experimental results indicating that $r\sim 0.5$. They later found,[12] however, that these results were due to the then unsuspected existence of an accommodation coefficient, so that there is no actual experimental measurement of r. From the fact, however, that direct measurement of the radiation from the cathode spot (process (3) Fig. 1) shows this to be almost negligible, it is evident that r is practically unity. Whatever error may be introduced in taking $r=1$ will be exactly corrected by introduction of the experimental value of heat loss by radiation in process (3).

Combining all these considerations, we have for process (1)

$$H(1) = (1-f)(aV_c + V_i - \phi_0)$$

(2) *Cooling by electron emission.* This process of cooling is too well known to require comment, since it is well known that the electron work function ϕ_- is a latent heat of evaporation. Expressing it as a negative heating process, we have

$$H(2) = -f\phi_-$$

(3) *Cooling by radiation* is expressed directly, in terms of the observed radiated energy per ampere·sec., by $H(3)=-R$.

(4) *Cooling by evaporation* of the material of the cathode is similarly expressed by $H(4)=-E$, in which E is the product of the mass of material evaporated per ampere·sec multiplied by its latent heat of evaporation.

(5) *Cooling by gas conduction and convection* is $H(5)=-C'$.

(6) *Cooling by conduction through the cathode* is $H(6)=-C$.

(7) *Heating by an external agency*, if any, is represented by $H(7)=H$.

(8) *Heating by energy derived by electrons in the cathode fall space and indirectly returned to the cathode* can be calculated as follows. The work done on an escaping electron is V_c. If part of this work is done in pulling the electrons out of the metal (as in Langmuir's theory), this part may be expressed by

[14] Compton and Van Voorhis, Proc. Nat. Acad. Sci. **13**, 336 (1927).

$(\phi_0-\phi_-)$, where ϕ_0 is the ordinary electron work function for negligibly small accelerating fields, and ϕ_- is the actual or "effective" work function. Thus the energy with which each electron is projected out of the cathode fall space is $V_c-\phi_0+\phi_-$.

Of the total energy $f(V_c-\phi_0+\phi_-)$ thus fed into the vapor, $(1-f)V_i$ must be used to produce the $(1-f)$ positive ions which return to the cathode. We shall see below that altogether $(1+\delta)$ times this number of ions must be formed, where $0<\delta<1$, since some of the ions are formed beyond the region of potential maximum and drift toward the anode, ultimately recombining. δ is the ratio of the number of ions thus going toward the anode to the number going toward the cathode. Thus we have $(1+\delta)(1-f)V_i$ energy used in producing positive ions.

Furthermore the probe electrode measurements prove that the electrons in the negative glow near the cathode possess a considerable mean kinetic energy $\bar{V}_-$. Thus the energy fed into the vapor by electrons from the cathode, which is not expended in producing ions or retained by the electrons, is $f(V_c-\phi_0+\phi_-)-(1+\delta)(1-f)V_i-\bar{V}_-$, where the factor f does not multiply $\bar{V}_-$ since we know that in the negative glow the fraction of current carried by electrons is unity within a fraction of a percent.

Let F represent that fraction of the energy, acquired by *unelectrified* carriers from the electrons which have moved through the fall space, which returns to the cathode (as by radiation, metastable and excited atoms, high temperature neutral atoms). We have already allowed in process (1) for the energy which is brought back by positive ions, and of course none is brought back by electrons. This remaining source of heating of the cathode is therefore given by

$$H(8) = F[f(V_c - \phi_0 + \phi_-) - (1 + \delta)(1 - f)V_i - \bar{V}_-].$$

Equilibrium. Equating to zero the sum of all these eight contributions to the heating, and solving for f, we obtain

$$f = \frac{aV_c + V_i - \phi_0 - (R + E + C + C' - H) - F[(1 + \delta)V_i + \bar{V}_-]}{aV_c + V_i - \phi_0 + \phi_- - F[V_c - \phi_0 + \phi_- + (1 + \delta)V_i]} \quad (1)$$

Supplementary relation. The above expression for $H(8)$ gives us another clue to the value of f. The expression in brackets is the amount of the energy with which the electrons are shot into the vapor which is not retained by them or used in ionization. It must of necessity be greater than zero, since we know that a considerable portion of such energy is used, for example, in producing metastable or other excited atoms. In fact, we shall later discuss reasons for believing that the ionization is principally of the two stage or cumulative type. Thus from $f(V_c-\phi_0+\phi_-)>(1+\delta)(1-f)V_i+\bar{V}_-$, we find

$$f > \frac{(1 + \delta)V_i + \bar{V}_-}{V_c - \phi_0 + \phi_- + (1 + \delta)V_i}. \quad (2)$$

Values of the terms are given in Table I.

TABLE I.

Quantity	Value	Reference
V_e	10 volts	Lamar and Compton[15]
V_i	10.4	Well known
ϕ_0	4.5	Kazda[16]
R	0.04	Güntherschulze[10]
E	2.21–0	" (see below)
C	2.68	"
C'	0.0	"
H	0.0	No external heating
V_-	1.5	Lamar and Compton[15]
ϕ_-	0–4.5	(see below)
F	0.5–1.0	" "
a	1–?	" "

$E=2.21$ is based on measurements by Güntherschulze of the rate of loss of mass of the cathode, together with the latent heat of evaporation of mercury at 123°C. However, Compton and Van Voorhis suggested[14] that some of the mercury may be lost as a spray thrown out mechanically by the agitation of the surface. Such loss would not involve cooling. Issendorff[17] has verified this experimentally and has shown that the actual amount of true evaporation from the cathode spot is practically negligible as a cooling process. (Much of the spray is subsequently volatilized in the arc stream by heat developed by recombination of electrons and ions on the surfaces of the droplets, but this is not a process which cools the cathode.) It appears from this that the true value of E lies much closer to 0 than to 2.21. As to the assumed temperature of 123°C, see discussion later in the paper.

$\phi_-=0$ to 4.5, depending on the extent to which the emission is due to the field, being 0 if due entirely to the field. Perhaps a rough approximation to the right value is given by finding the effective work function which would give thermionic emission of 4000 amp·cm^{-2} at 123°C, which is $\phi_-=0.31$ volt.

F has a more restricted significance than in previous discussions owing to the more complete character of the present analysis. If the energy carried back to the cathode by unelectrified carriers is in the form of unabsorbable radiation, we should expect $F=0.5$, since the cathode subtends half the solid angle about the origin of radiation, or less than 0.5 if there is reflection at the cathode surface. Actually, however, we know such radiation to be small (see Table I). If the energy gets back by any diffusion process, as by metastable atoms or by resonance radiation, then much more than half the energy will return to the cathode since the mean free path of the diffusing particles is considerably less than the distance from the cathode to other boundaries of the vapor. Since this condition is amply fulfilled in the mercury arc, we have $1.0>F>0.5$, and it is extremely probable that F is very nearly equal to 1.0.

a has not been measured for mercury, but we should expect it to be $1.0>a>0.9$, since in other gases a approaches unity with increasing atomic weight.

[15] Lamar and Compton (preceding paper in Phys. Rev.).
[16] Kazda, Phys. Rev. **26**, 643 (1925).
[17] Issendorff, Phys. Zeits. **29**, 857 (1928).

Results for the various assumptions are given in Table II. Note first that f_2 involves the uncertain factors δ and ϕ_- and depends only on the direct application of the Energy Principle. Note also that the known fact that impact ionization processes are never very close to 100 percent efficient shows that the true value of f must be *considerably* larger than the lower limit set by f_2. The values in parentheses are impossible values either because $f_1 < f_2$, or because f_1 is negative or greater than unity.

TABLE II. $f_1 = f$ by *Eq.* (ϕ); $f_2 = f$ by Eq. (2).

			$\phi_-=0.0$			$\phi_-=0.31$			$\phi=4.5$		
		δ	1.0	0.5	0.0	1.0	0.5	0.0	1.0	0.5	0.0
		f_2	0.85	0.81	0.75	0.84	0.80	0.73	0.73	0.67	0.58
E	a	F	f_1	f_1	f_1	f_1	f_1	f_1	f_1	f_1	f_1
0.0	1.0	0.0	(0.83)	0.82	0.82	(0.81)	0.81	0.81	(0.64)	(0.64)	0.64
		0.1	(0.82)	0.82	0.83	(0.81)	0.81	0.82	(0.63)	(0.64)	0.65
		0.2	(0.82)	0.83	0.85	(0.80)	0.82	0.84	(0.61)	(0.64)	0.67
		0.5	(0.74)	0.86	0.91	(0.70)	0.84	0.89	(0.41)	(0.61)	0.71
		0.6	(−17.0)	0.90	0.95	(−0.71)	0.87	0.93	(−11.5)	(0.51)	0.74
		0.7	0.96	(1.08)	(1.02)	0.99	0.98	1.00	(4.00)	(0.49)	0.79
		0.8	0.91	(0.51)	( )	0.92	(0.55)	( )	(1.10)	(6.25)	0.90
		0.9	0.89	(0.70)	( )	0.89	(0.72)	( )	0.94	0.83	(1.21)
		1.0	0.89	(0.75)	( )	0.89	(0.75)	( )	0.89	0.75	( )
0.0	0.9	0.0	(0.82)			(0.80)			(0.63)		
		0.1	(0.81)			(0.79)			(0.61)		
		0.2	(0.80)			(0.78)			(0.58)		
		0.5	(0.59)			(0.54)			(0.26)		
		0.8	0.93			0.93			(1.08)		
		0.9	0.90			0.90			0.95		
		1.0	0.89			0.89			0.89		
2.21	1.0	0.0	(0.69)	(0.69)	(0.69)	(0.68)			(0.54)	(0.54)	(0.54)
		0.1	(0.66)	(0.67)	(0.68)	(0.64)			(0.50)	(0.52)	(0.53)
		0.2	(0.61)	(0.65)	(0.68)	(0.60)			(0.46)	(0.49)	(0.53)
		0.5	(−0.07)	(0.50)	(0.63)	(−0.06)			(−0.04)	(0.33)	(0.50)
		0.8	(1.34)	(2.70)	(0.47)	(1.35)			(1.62)	(23.0)	(0.36)
		0.9	(1.17)	(1.42)	(0.02)	(1.18)			(1.25)	(1.70)	(0.15)
		1.0	(1.09)	(1.09)	(—)	(1.09)			(1.09)	(1.09)	(−)
0.44	1.0	0.0	(0.80)			(0.79)	(0.79)	0.79	(0.62)		
		0.1	(0.79)			(0.78)	(0.79)	0.79	(0.61)		
		0.2	(0.78)			(0.76)	(0.79)	0.80	(0.58)		
		0.5	(0.58)			(0.55)	0.86	0.84	(0.32)		
		0.8	0.99			(1.01)	0.99	1.00	(1.21)		
		0.9	0.94			0.95	0.85	(1.33)	1.00		
		1.0	0.92			0.92	0.83	( )	0.92		

Conclusions. A survey of Table II shows, first of all, the futility of attempting to determine the fraction f by heat balance methods, since the unknown parameters E, a, F, leave a great range of possibilities. Nevertheless some interesting information can be obtained.

Obviously no adjustment of ϕ_-, a, F, δ will give possible results if E is as large as Güntherschulze's value 2.21, which checks the later estimates described above, which make $E << 2.21$.

It is probably hopeless to try to measure F and δ. Physical considerations, mentioned above, however, place $1.0 > F > 0.5$ (with F probably nearer 1.0 than 0.5. Similarly we shall see that $1.0 > \delta > 0$.

With these possibilities in mind, we see from Table II that the most probable values of f arise from cases where *both the numerator and denominator of Eq.* (1) *are negative*,—which means that a very appreciable role is played by the heating effect of energy which reaches the cathode by unelectrified carriers, an observation which is suggestive of a considerable concentration of

metastable atoms and of cumulative ionization. More direct evidence of this appears later in the paper.

In the light of this study it seems hopeless to prove or disprove the Langmuir theory by heat balance arguments. *This analysis shows for the first time, however, that the heat balance may be made consistent with Langmuir's theory and with the known facts of ionization* by making the most reasonable assumptions regarding the unknown factors F and δ. In order to make the considerations still more precise, it is important to measure the accommodation coefficient a for Hg ions at a Hg surface and to obtain a more reliable estimate of evaporation E under conditions in which the other thermal quantities are also measured. Thus we may assume Langmuir's theory, with its very small value of ϕ_-, on the basis of its reasonable character and the absence of evidence for any other adequate mechanism.

Temperature and Vapor Pressure at Cathode

The temperature and vapor pressure at the cathode can be calculated if the rate of evaporation from the cathode is known. Early attempts to measure this led to erratic and large values. Schaefer[18] found 36.7 $(10)^{-3}$g·amp. sec^{-1}, and Güntherschulze[10] 7.2 $(10)^{-3}$g·amp.$^{-1}$ sec^{-1}. Compton and Van Voorhis' suggestion[14] that these large values arise from mechanical spray was verified by Issendorff,[17] who found <1.3 $(10)^{-3}$ g·amp.$^{-1}$ sec^{-1}. Recently Kobel[19] devised a means for holding the cathode spot quiescent and found the rate of evaporation to be 0.017 $(10)^{-3}$ amp.$^{-1}$ sec^{-1}. Since this lies within Issendorff's limits, and since a quiescent spot would be expected not to eject spray, we shall take this as the best value at present available. (The device for holding the spot quiet may have made this value too small, but several considerations indicate that such an error is small, if present.) Kobel's average current density was 1912 amp·cm^{-2}, hence the rate of evaporation was 0.0325 gm·cm^{-2}.

It must be observed, however, that these values refer only to the *net* rate of escape of Hg atoms. The true rate of evaporation is larger than this, but a certain portion of the evaporated atoms return to the cathode as ions. The true rate of evaporation M can be equated to the observed rate M_0 plus the rate of return of ions to the cathode, which is 0.00209 $(1-f)$ g·amp.$^{-1}$ sec^{-1}. (0.00209 is the electrochemical equivalent of Hg). If we express this in terms of evaporation per cm^2, we have

$$M = M_0 + 0.00209(1 - f)j, \tag{3}$$

where j = current density. From the familiar kinetic theory relations

$$n = \tfrac{1}{4}N\bar{v}, \quad p = \tfrac{1}{3}Nm\bar{v}^2 = NkT, \quad M = nm$$

we find

$$p^2 = \frac{16}{3}\frac{M^2kT}{m} \text{ dynes} \cdot \text{cm}^{-2}, \tag{4}$$

where m is the mass of an atom in grams.

[18] Schaefer, Diss. Darmstadt (1910).
[19] Kobel, Phys. Rev. **36**, 1636 (1930).

If the experimental values of M from Eq. (3) are substituted into Eq. (4), an infinite number of pairs of possible values of pressure p and temperature T is found. Only one of these pairs of values, however, satisfies the vapor pressure relation between p and T. Thus Eq. (4) together with the vapor pressure equation, serve simultaneously to fix unique values of T and p. This value of T is the temperature of the cathode spot and from p and T we can find the value of atomic and electronic mean free paths just outside the cathode.

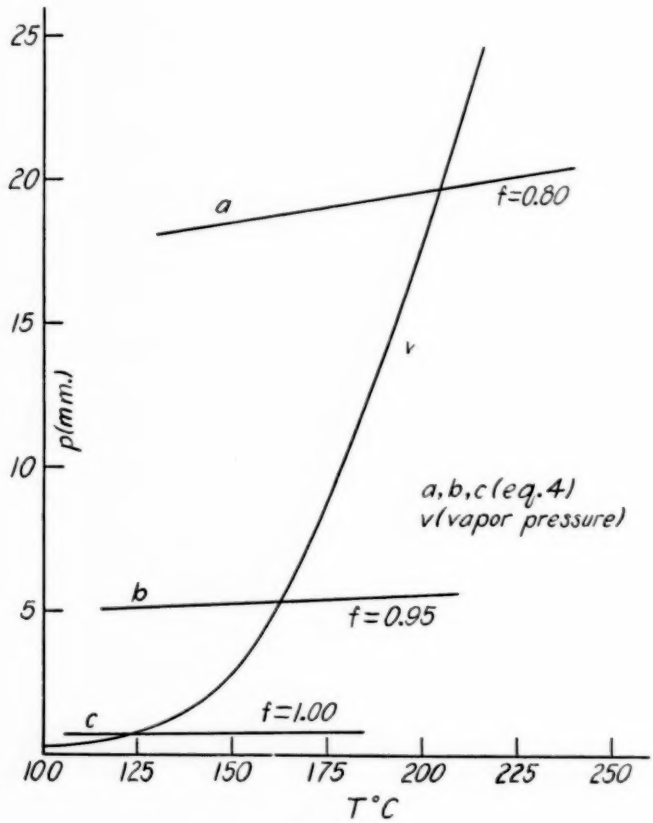

Fig. 3.

Here, as before, uncertainty in f prevents us from drawing definite conclusions, but here again we can set certain limits with considerable assurance. If ionization is cumulative in two stages, not more than one ion can be formed

TABLE III.

f	p	T	λ(electron)[20]	d_e
1.00	0.75 mm	123°C	0.0026 cm	(0.000176) cm
0.95	5.4	167	0.00033	0.000039
0.80	19.6	202	0.000084	0.000019

[20] Constants from Compton and Langmuir, Rev. Mod. Phys. **2**, 208 (1930).

for every two electrons, and if half the ions move toward the anode, recombining ($\delta = 1$), we must have $f > 0.8$. Table III shows the results of three assumptions, the values being taken from Fig. 3. For comparison there are shown also the corresponding values of thickness of cathode fall space, calculated as in the preceding paper.

Three important facts are derived from this consideration of rate of evaporation: (1) the surface temperature of the cathode spot cannot exceed about 200°C; (2) the vapor pressure there is considerably less than the value of about one atmosphere recently assumed;[21] (3) the electron mean free path is, in any case, considerably longer than the thickness of the cathode fall space, a fact which justifies several simplifying assumptions such as the applicability of the simple space-charge equation in the fall space.

Question of high-speed ejection of vapor. Tangberg[22] for a copper arc and Kobel[19] for a mercury arc have called attention to the relatively large pressure on the cathode spot and have interpreted it as indicating very high speeds of evaporating atoms, speeds characteristic of temperatures of the order of 500,000°K! Among the physical difficulties of this interpretation may be mentioned the inconsistency between such a temperature and the observed rate of evaporation which, as we have seen, indicates a surface temperature of not more than 200°C. Compton[23] suggested that a more reasonable interpretation of this pressure is to be found in the existence of an "accommodation coefficient" for ions which strike and are neutralized at the surface—this accommodation coefficient having been inferred for He, Ne and A ions from thermal measurements at cathodes by Van Voorhis and Compton[12] and later measured directly for He ions by Lamar.[24]

For the mercury arc, the pressure resulting from an accommodation coefficient $a < 1.0$ may be calculated thus, per cm²:

Positive ion current at cathode	$j(1-f)$ amp.
Mass of positive ions striking cathode per sec	$0.00209\, j(1-f)$ g
Number of positive ions striking per sec	$0.63(10)^{19}\, j(1-f)$
Kinetic energy of incident ion	$1.59(10)^{-11}$ erg
Total kinetic energy of ions striking per sec	$1.00(10)^{8}\, j(1-f)$ erg
Total kinetic energy of neutralized ions leaving cathode per sec	$1.00(10)^{8}\, j(1-f)\,(1-a)$ erg
Total momentum of neutralized ions leaving cathode per sec	$647\, j(1-f)\,(1-a)^{1/2}$ dyne.

This last quantity is the pressure, provided the neutralized ions leave normally to the surface. We should rather expect the escaping neutralized ions to be scattered in all directions, and in fact Lamar's results indicate this

[21] Güntherschulze, Zeits. f. Physik **11,** 74 (1922); Langmuir, Science **58,** 290 (1923); Compton, Summer Convention A.I.E.E. (1927).

[22] Tanberg, Phys. Rev. **35,** 1080 (1930).

[23] Compton, Phys. Rev. **36,** 706 (1930). (In this paper there is a numerical error which arose through taking an incorrect value for the electrochemical equivalent of Hg, but which, qualitatively, does not vitiate the argument).

[24] Lamar (to be reported at Washington Meeting of the Amer. Phys. Soc.) and published in the Physical Review.

in the case for He ions. In this case we must use the mean normal component of momentum, which gives just half the above values. We thus have

$$\begin{aligned} p &= 0.66j(1-f)(1-a_n)^{1/2}\text{g}\cdot\text{cm}^{-2} \\ p &= 0.33j(1-f)(1-a_r)^{1/2} \end{aligned} \tag{5}$$

depending on whether we assume a_n (normal escape) or a_r (random escape).

Kobel's results gave an average pressure of 5.75 cm Hg (78.2 g·cm^{-2}) on the cathode spot whose average current density was 1912 amp·cm^{-2}. Substituting these values in Eq. (5) we obtain the relations shown in Table IV.

TABLE IV.

f	0.50	0.60	0.70	0.80	0.90
a_n	0.985	0.98	0.96	0.90	0.62
a_r	0.95	0.92	0.84	0.60	(—)

Since, as we have seen, experimental evidence points to a_r rather than a_n, we see that this analysis suggests that the accommodation coefficient a for Hg ions is less than the value, nearly unity, suggested by its high atomic weight, taken in conjunction with the known values of a for He, Ne and A. This again emphasizes the desirability of making a direct measurement of a for Hg ions.

MECHANISM OF IONIZATION

The fact that the cathode drop is so constantly close to 10 volts, independently of current, vapor pressure, etc., over the entire range in which a Hg arc can be struck from a liquid Hg cathode, suggests that this value is fixed by some characteristic process in the arc mechanism. It has been quite generally assumed that this process is the ionization of the Hg atoms by electron impact, and that the significance of 10 volts is, roughly, the ionization potential 10.4 volts. There are, however, three serious and probably insuperable difficulties besetting such an interpretation, as follows.

(1) The probability of ionization by an electron of 10.4 volts energy, or even a few volts more, is so small that it is difficult thus to account for the production of the requisite number of positive ions. (2) The present more refined measurements of cathode drop point to a value *less*, rather than exceeding, 10 volts, the best estimate being 9.9 volts, which makes the assumption of direct impact ionization still more unsatisfactory. (3) *If the electrons are pulled out of the cathode by the field*, the field thus does work $\phi_0 = 4.5$ volts in pulling them out, so that *the kinetic energy gained by the escaping electron is only* $9.9 - 4.5 = 5.4$ *volts, which is far insufficient to permit ionization by single impact.*

The obvious escape from these difficulties is to adopt the theory that *ionization is caused in two stages*, which is at once seen to be in excellent accord with various related facts. The electron energy is very close to the value necessary to produce excited or metastable atoms, and to ionize them when formed. We know that, unlike ionization by single impact, these processes have a high probability when the energy of the impacting electron is only

slightly in excess of the minimum energy required for the process. Furthermore, experiments with low voltage arcs have proved that the favorable conditions for arcs to operate by such cumulative ionization are large current density and vapor pressure of at least the order of 1 mm, both of which conditions are amply fulfilled in the mercury arc. *Thus it would be very surprising if the ionization were not of the cumulative type.* The reason for not having adopted this interpretation sooner was principally the difficulty, in preceding analyses of the situation, of justifiying a value of f large enough to be consistent with it, and secondarily the erroneous apparent significance of a cathode drop so nearly equal to the ionizing potential.

Electrical Conditions Near Cathode

In Fig. 4, let the ordinates of curve N represent the relative numbers of electrons, projected out from the cathode, whose free paths terminate by

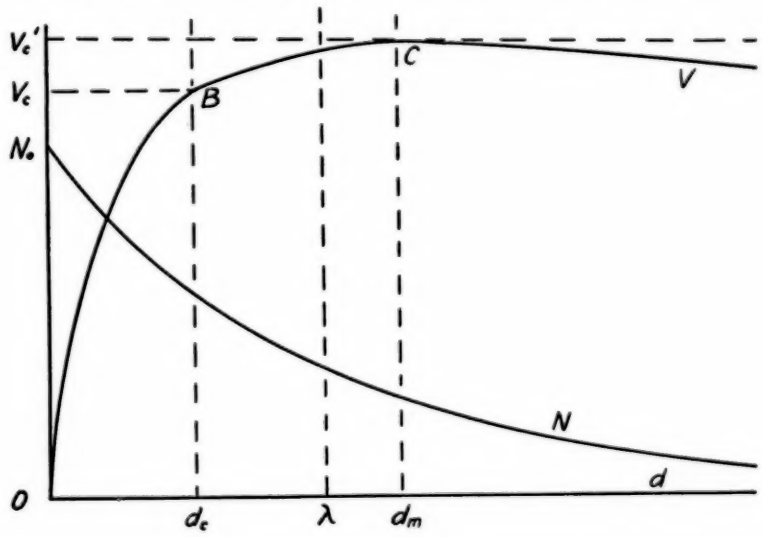

Fig. 4.

collisions at distances d. Since, as we have seen, the thickness of the fall space d_c is less than the mean free path λ, we may consider these as projected out with uniform velocities corresponding to the kinetic energy $V_c - \phi_0$. The rate of production of ions or excited atoms will therefore also be proportional to the ordinate of curve N at each distance from the cathode.

Every region of intense ionization tends to be a region of potential maximum, owing to the fact that electrons diffuse away from it more rapidly than do positive ions. There is therefore, a little way in front of the cathode, a region of potential maximum C. As a first approximation, this may be taken as being at the distance of one mean free path from the cathode, since this is the mean position at which ionization occurs.

From this region of potential maximum C, positive ions are forced by the field *in both directions*, half moving in to the cathode and half moving out

toward the anode and eventually combining with electrons. Since the cathode is so much nearer than the anode to this region of potential maximum, the concentration gradient on the cathode side must be greater than that of the anode side, which would tend to displace the region of potential maximum away from the cathode. On the other hand, the fact that ionization occurs at a more rapid rate nearer the cathode, as shown by curve N, tends partially to offset this displacement. The extent of this displacement determines the amount by which δ in Eqs. (1, 2) differs from 1.0.

The net result of these actions, including the action of space charge within the space-charge sheath (cathode fall space) is shown diagrammatically by curve V. The space charge equation applies within the distance d_c, to the point B. Between B and the potential maximum, the plasma considerations developed by Tonks and Langmuir[25] apply. Beyond C there is ambipolar diffusion toward the anode by both electrons and ions.

There is obviously a small uncertainty in the meaning of "cathode drop". The drop across the space-charge sheath to the point B is the quantity which is significant in estimating the field at the cathode. The drop to the point C is the maximum potential drop available to produce ionization. The drop to some point beyond C—i.e., to the point of nearest approach of an exploring electrode, is the nearest point to which the drop can be measured experimentally, as in the preceding paper.

In conclusion, it may be noted that this analysis indicates that the limits of uncertainty in the values of f, d_c and field at cathode may be reduced by more careful measurements of thermal relationships and of accommodation coefficient, but that the accuracy of an absolute evaluation of these quantities is limited principally by our inability accurately to measure or estimate two factors: the fraction F of the energy, imparted by electrons to unelectrified carriers, which goes to the cathode; and the fraction $1/(1+\delta)$ of the positive ions formed near the cathode which go to the cathode.

[25] Tonks and Langmuir, Phys. Rev. **34,** 876 (1929).

THE ELECTRODELESS DISCHARGE IN MERCURY VAPOR

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(Received March 16, 1931)

Abstract

A method is described for studying the characteristics of the components of the electrodeless discharge in mercury vapor. A Hartley oscillator is used to excite the discharge, oscillating currents up to 45 amps. being obtained at frequencies from 5×10^6 to 12×10^6 oscillations per second. Shield experiments have been performed which clearly show the distinction between the dull glow discharge which is considered electric in its origin and the bright glow discharge which is shown to be electromagnetic in its origin; the dependence of the bright glow on the dull glow or on the effect of some ionizing agent is proved. The variation of the current necessary to start the discharge with the pressure of the mercury vapor has been investigated fully over the pressure range 0.002 to 0.2 mm of mercury. Curves are drawn and analyzed in terms of J. J. Thomson's electromagnetic theory of the discharge and Brasefield's electric theory. It is shown that neither theory is sufficient to explain the experimental facts; the predictions seem to hold for the bright glow with fair agreement but fail markedly with the dull glow.

Introduction

TWO opposing theories have been advanced in recent years to explain the nature of the "electrodeless" discharge which occurs under proper excitation in a gas or vapor at low pressure. The usual arrangement is to insert the bulb containing the gas in a coil in which high frequency currents are flowing.

J. J. Thomson[1] has contended that the discharge is due to the alternating e.m.f. induced around the inside periphery of the discharge tube by the varying magnetic field of the coil. Townsend and Donaldson[2] however have strongly supported the view that the discharge is caused by the "electric forces"[3] between the ends of the coil. This second view is also held by those who have worked with external electrodes, for example Brasefield.[4]

In an attempt to reconcile the two explanations MacKinnon[5] constructed an exciting circuit which could be energized by either damped or undamped oscillations, for the reason that Thomson had used only damped oscillations while Townsend and Donaldson had used only undamped oscillations. From his experiments, MacKinnon concluded that the discharge was of "electromagnetic" origin when excited by the damped oscillations of Thomson and

[1] J. J. Thomson, Phil. Mag. **32,** 321, 450 (1891); **44,** 293 (1897); **4,** 1128 (1927).

[2] Townsend and Donaldson, Phil. Mag. **5,** 178 (1928).

[3] The term "electric forces" is used here to represent those forces due to the fact that two parts of the coil are at different potentials. For such a force the usual term "electrostatic" is here obviously a misnomer.

[4] Brasefield, Phys. Rev. **35,** 1073 (1930); **37,** 82 (1931).

[5] K. A. MacKinnon, Phil. Mag. **8,** 605 (1929).

"electric" when excited by the undamped oscillations of Townsend and Donaldson. With large currents in the undamped oscillator coil he was able to obtain a very bright glow, not reported by Townsend and Donaldson, which he thought was related to the "ring" discharge of Thomson. This led him to believe that the electromagnetic type of discharge occurred with the damped oscillations because the instantaneous coil currents were very large, and that the undamped oscillations would also cause the characteristic "ring" discharge of the damped case if the gas used had a sufficiently low ionizing potential. The results of the present work support MacKinnon's view in many details.

An ordinary Hartley circuit was used as a generator of the high frequency oscillations employed in the experiments to be described. The resistance of the circuit was kept low by the use of copper tubing for leads and inductance coils while the ratio of capacity to inductance was high; the result was the generation of large currents in the oscillator coil which also acted as the exciting coil for the discharge; thus currents of 45 amps. at frequencies from 5×10^6 to 12×10^6 cycles per second were easily obtained. These currents were measured by a Weston thermo-ammeter placed directly in the circuit between coil and condenser or by a current transformer and thermo-ammeter as described by Campbell and Dye.[6] All frequencies were measured by a General Radio precision wave-meter.

Over the whole pressure range studied (0.002 to 0.2 mm of mercury) the authors have observed both types of discharge described by MacKinnon; over parts of the range, however, special precautions were necessary to separate them. Mercury vapor was used in the bulb throughout the investigation except where indicated otherwise. The general procedure was as follows: The pressure in the bulb was held constant and the coil current gradually increased; at a critical value of the current a bluish white "dull glow" appeared inside the tube. When the current was increased to a second critical value, the discharge suddenly changed into an intense "bright glow"; at the same time, a large amount of power was drawn from the oscillator. At certain pressures this "bright glow" assumed the form of a ring around the inside periphery of the tube, in appearance very similar to the familiar "ring" discharge.

When no discharge was excited on inserting the tube in the coil, no change occurred in the oscillating circuit. When the dull glow was excited, no change occurred in the circuit nor was the discharge tube heated appreciably. But when the bright glow was strongly excited, the oscillating current decreased greatly, the plate current increased, the frequency remained the same and the bulb was heated appreciably.

Effect of a Shield

The "dull glow" has been excited readily either inside or outside the coil; in fact at certain pressures, it has appeared whenever the bulb was brought anywhere near the oscillator. This action in itself indicates the "electric"

[6] Campbell and Dye, Proc. Roy. Soc. **A90**, 621 (1914).

nature of this type of discharge. To investigate the case further a metallic shield was made by pasting narrow strips of tin-foil parallel to each other on a piece of paper and then connecting them together at one end by a transverse strip of foil. The paper was then rolled into a hollow cylinder with the axis parallel to the strips and the ends open. When this cylinder surrounded the bulb it caused very little electromagnetic loss due to eddy currents but served as an excellent shield against "electric forces." When the pressure and coil current were suitable for the excitation of the "dull glow," the presence of the shield always caused the glow to disappear whether the discharge tube was in the coil or outside. The glow never reappeared as long as the shield remained interposed between the tube and the coil, no matter how great the coil current was made (in our case up to 45 amps.).

If the "bright glow" had been existed strongly in the tube and the shield was inserted, the glow was apparently unaffected. If the bright glow was stopped however by a reduction of the current, it could not be made to reappear so long as the shield was in place even though the current reached the maximum of 45 amps. These experiments were repeated with a second cylindrical shield with closed ends; the results were the same.

When damped oscillations of approximately the same frequency as the undamped oscillations were used for excitation, the dull glow could be obtained only outside the coil; the shield affected it in exactly the same manner as before. The bright "ring" discharge which appeared inside the coil behaved toward the shield identically as did the bright glow of the undamped case.

When the conditions were right for maintaining the bright glow without a shield, it could be started and maintained inside the shield by exposing the tube momentarily to x-rays, or with a quartz discharge tube, to the radiation from a mercury arc in quartz. If a small ball of mercury was in the tube, the bright glow could be started similarly by simply twirling the tube and thus generating a faint glow of triboluminescence around the ball of mercury.

All of the above shield experiments have been repeated for air and carbon monoxide with similar results.

Variation of Starting Current with Pressure

The variation of the current necessary for starting the discharge in mercury vapor with changing pressure was very difficult to observe precisely. The external condition of the tube, slight impurities in the vapor and small amounts of liquid mercury all affected the starting current and the results at first were so erratic that it seemed as though no generalization could be made. Determination of the pressure was difficult as the measurement of the temperature of a furnace in which the bulb and coil were placed was not satisfactory because of the sudden rapid increase in temperature in the closed space when the oscillating current was turned on. A thermometer placed anywhere in the field of the coil proved unreliable.

Reproducible results were finally obtained with the following apparatus and procedure. The discharge tube is shown in Fig. 1; the bulb *a* was placed within the oscillator coil and both were enclosed in a transite box and heated

by a blast of hot air; this furnace could be adjusted to any desired temperature from 120°C to about 200°C and maintained constant within a few degrees. The well *b* was outside of the furnace in a constant temperature bath which could be varied from 0°C to 100°C; it contained liquid mercury. Thus the pressure of the mercury vapor in the bulb was determined by the temperature of the mercury in the well, as read on a thermometer placed in tube *c*. The pressure corresponding to a given temperature was taken from a curve plotted from the data given by Kaye and Laby.

At the start of a run, the furnace was first raised to a temperature of say 180°C and kept there for about half an hour with the bulb and coil in place and the mercury well at a low temperature; this action insured that all the liquid mercury was evaporated from the bulb itself. The temperature of the well was then raised by adjustment of the constant temperature bath to the

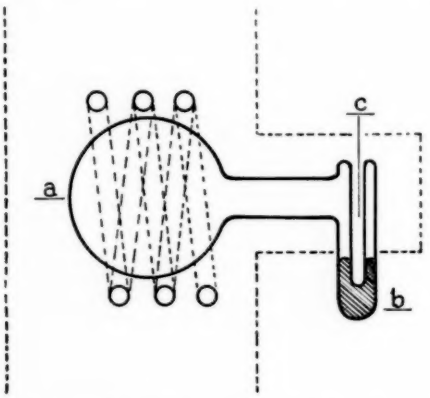

Fig. 1. The experimental bulb made of Pyrex. The broken lines show the position of the transite walls of the furnace.

value corresponding to the pressure at which the run was to be made. After a wait of about fifteen minutes at this temperature, readings of the starting current were taken at one-minute intervals. When these showed no consistent change, the average of six or more consecutive readings was taken as the starting current.

Table I shows a typical set of readings for starting currents; I_1 is the start-

TABLE I. *Currents necessary to start the electrodeless discharge.*

Frequency = 7.2×10^6 cycles per second. Temperature of furnace = 184°C. Temperature of the mercury well = 75.5°C. Pressure of mercury vapor in discharge tube = 0.066 mm of mercury.

	1	2	3	4	5	6	Average
I_1 amps (dull glow)	5.00	4.80	4.85	5.00	4.90	4.95	4.91
I_2 amps (bright glow)	6.60	6.65	6.65	6.65	6.65	6.65	6.65

ing current for the dull glow and I_2 that for the bright glow. The values of I_2 are more consistent than those of I_1; this was generally the case.

Figure 2 gives the curves illustrating the variation of starting current with pressure at a frequency of 7.2×10^6 cycles per second. Curve *bcdfh* is for the bright glow and curve *acefg* for the dull glow; all pairs of curves taken were very similar to these in shape. The minima at *b* and *e* occurred at the same pressures for the different curves and at about the same currents but the rest of the curve was often shifted along the current axis. Within the pressure range from *c* to *f* of Fig. 2 the starting currents of the two discharges followed each other as described above. To the left of *c* and to the right of *f*, the bright discharge appeared at points on the curve *ac* and *fg*; the dull glow did not precede the bright glow in these regions. When the power supplied to the oscillator was decreased however the bright glow was made to disappear but the dull glow remained. When the power was again increased, the dull glow

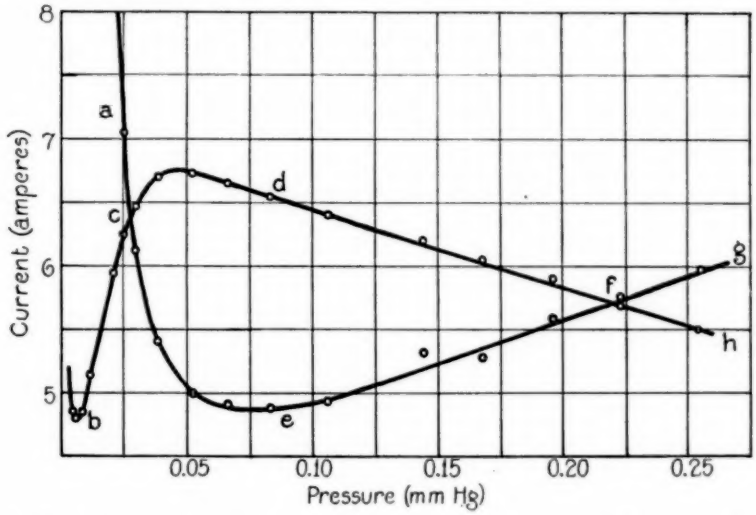

Fig. 2. Typical curves showing the variation of starting current with pressure in mercury vapor. Curve *bcdfh* is for the "bright glow" and curve *acefg* is for the "dull glow"; the former appears again as D_1 in Figs. 3 and 3a and the latter as D_1' in Fig. 3.

still being on, the bright glow reappeared at a considerably lower current than at first, corresponding to some point in the region *bc* or *fh*. Since our experiments with the shield have shown that the bright glow does not appear at any pressure unless preceded by the dull glow or by some external source of ionization, we have taken *bcdfh* as the true starting current curve for the bright glow, and *acefg* for the dull glow. Both types of discharge exist therefore over the whole range of pressures and may be started or stopped at will.

The minimum at *b* of the bright glow appears again in the curves D_1 of Figs. 3 and 3a; the last curve shows particularly how definite the minimum is.

Discussion of Results

Figs. 3 and 3a give the results of one set of experiments; many others were obtained like them. The full line curves *A*, *B*, *C* and *D* show the variation of starting current with pressure for the bright glow while the dotted curves

A', B', C' and D' are for the dull glow. Curves A_1, A_2 and A_3 were all taken at a frequency of 11×10^6 cycles per second; the oscillator coil had an induc-

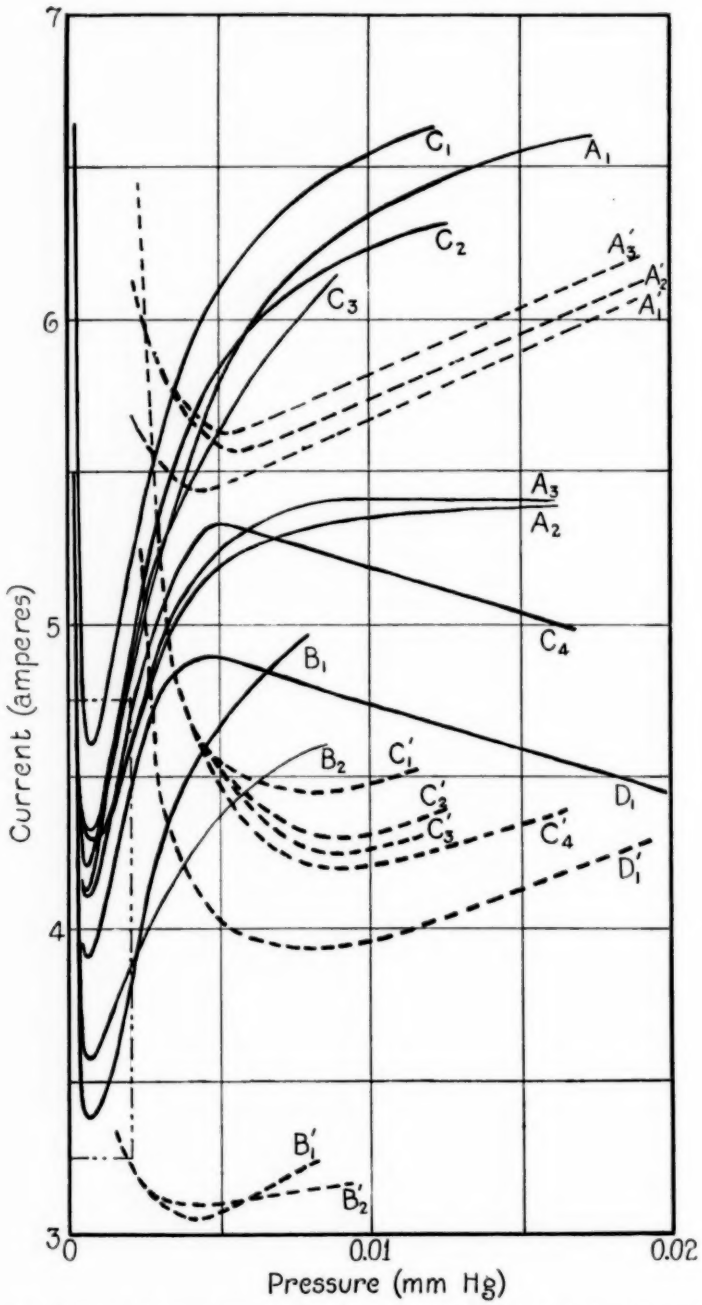

Fig. 3. A collection of curves illustrating the effect of changes in inductance and frequency of the oscillating circuit on the minimum starting current; the full lines are for the "bright glow" and the broken lines for the "dull glow"; the curves similarly labelled, e.g., A and A' were taken simultaneously. The region to the left enclosed by the chain lines is enlarged in Fig. 3a.

tance of 6.84×10^{-7} henries. Curve A_1 was taken on June 11 after the tube had been operated for a considerable period previously at a frequency of a 7.2×10^{6} cycles per second. The minimum at 0.0028 mm of mercury is very definite but is the only case in which such a low pressure minimum has been observed; the minimum at 0.0070 mm has therefore been chosen as the proper minimum for comparison with the other curves; no explanation can be offered at this time for the appearance of the two minima. Curves A_2 and A_3

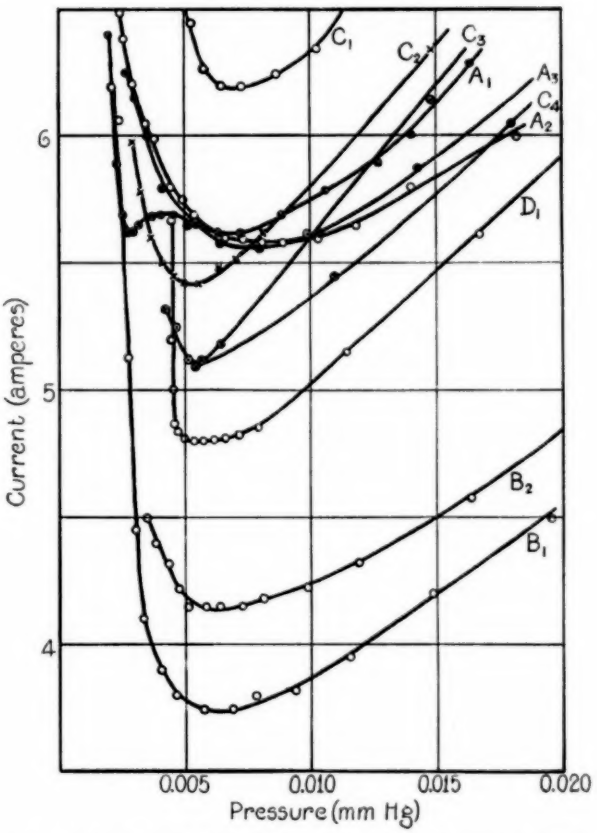

Fig. 3a. An enlarged view of the minima of the "bright glow" curves to show how sharply the minimum currents are defined.

were obtained on June 12. Figure 3a shows that their minima fall at a pressure of 0.0085 mm.[7]

Curves B_1 and B_2 were obtained on June 13; the frequency was kept at 11.0×10^{6} cycles per second as for the curves A but the inductance was increased to 10.4×10^{-7} henries. The minima for B_1 and B_2 are seen to fall at

[7] A comparison of curve A_1 with A_2 and A_3 shows that the first curve taken at a given frequency after the discharge tube has been run at a lower frequency results in a displacement of the minimum to a lower pressure than occurs with succeeding curves taken under otherwise identical operating conditions. The coil currents at the minima for A_2 and A_3 are less than for A_1; this whole behavior is typical.

a lower pressure than with the curves A, the value being 0.0065 mm. The "electromagnetic" theory of Thomson and the "electric" theory of Brasefield (for external electrodes) demand that the ratio of the frequency to the pressure at which the minimum occurs should be a constant; here, however, a shift takes place in the pressure at which the minimum occurs without a change of frequency but with a change of inductance. The values of the coil current at the minima are considerably lower with the curves B than with the curves A; this may be accounted for in terms of the change in inductance from 6.84×10^{-7} henries in the latter case to 10.4×10^{-7} henries in the former; the coils were of two and three turns, respectively. The magnetic field at the minimum should be

$$H_0 = \frac{2}{a}\left(\frac{2V}{e/m}\right)^{1/2}$$

according to Thomson, where V is the effective ionization potential for the gas and a the radius of the bulb; thus the starting current at the minimum should depend only on the gas, the bulb and the coil. The approximate value of the field inside of a solenoid is $H = 2\pi ni\ (\cos\theta_1 - \cos\theta_2)$ (see Starling 5th Edition p. 229); the coil current at the minimum should thus have been 16.8 amps. for curves A and 10.4 amps. for curves B, on the assumption further that the ionizing potential is 10.4 volts. If the effective ionizing potential is taken as 5.5 volts, these values become 12.2 amps. and 7.6 amps., respectively. Actually the currents were about 5.5 amps. for curves A and about 4.0 amps. for curves B.

The electric field at the minimum should be

$$E_0 = \pi f\left(\frac{2V}{e/m}\right)^{1/2}$$

according to Brasefield.[4] The shield experiments have given evidence of only diametral electrical fields; the recent experiments of Knipp[8] seem to confirm this observation. If this is the case

$$E_0 = \frac{\pi fL}{2Nr} I_0$$

where f is the frequency of the oscillation, L is the inductance of the coil, r is its radius and N the number of turns; I_0 is the peak value of the minimum starting current; this approximation for E_0 is based on the assumption of a linear drop in potential around the coil; a sine distribution leads to results of the same order. In effective amps. the above result becomes

$$I = \frac{2Nr}{1.414L}\left(\frac{2V}{e/m}\right)^{1/2}.$$

The coil current at the minimum should thus have been 2.24 amps. for curves

[8] Bulletin of the American Physical Society Vol. 6, number 1, p. 22, abstract 35, February 10, 1931.

A and 1.99 amps. for curves B, on the assumption that the ionizing potential is 10.4 volts. If the effective ionizing potential is 5.5 volts, these values become 1.63 amps. and 1.45 amps., respectively. The currents were actually about 5.5 amps. for curves A and 4.0 for curves B.

The observed values of the currents are of the same order of magnitude as the calculated values on either theory although the electromagnetic theory values are about twice as large as those observed and the electric theory values are between one fourth and one third as great, when the effective ionizing potential is taken as 5.5 volts. The electromagnetic theory predicts a change in the minimum current from curves B to curves A, the calculated ratio being 0.62. The electric theory predicts for diametral fields a shift corresponding to the ratio 0.89. The ratio of currents actually observed is 0.71.

Curves C_1, C_2, C_3 and C_4 were run in that order on June 14. Curve C_1 shows a minimum at a pressure of 0.0075 mm of mercury while the minima for the other three curves fall at a pressure of 0.0055 mm. The inductance was the same as for curves B, 10.4×10^{-7} henries, but the frequency had been lowered from 11.0×10^6 cycles per second to 7.2×10^6 cycles per second.[9] The ratio of the frequency to the pressure at the minimum for curve A_2 or A_3 and curve C_2, C_3 or C_4 is a constant within the limit of experimental error as predicted by both theories:

$$\frac{11.0\times10^6}{0.0085}=1295\times10^6;\quad \frac{7.2\times10^6}{0.0055}=1310\times10^6.$$

The ratio of inductance to capacity in curves A and C was constant. For curve B_1 or B_2 and curve C_2, C_3 or C_4 the ratios of frequency to pressure at the minimum are obviously not the same; the change in frequency resulted from a change in capacity in the circuit, the inductance remaining the same. Both theories predict that the coil currents at the minima for curves B and curves C should be equal as they are shown to be independent of the frequency. While successive values for curves B are increasing and those for curves C are decreasing, the values for the lower frequency are definitely higher than for the higher frequency.

Curve D was taken in an early set of experiments on May 22 and is included to show how well the results agree even after a lapse of time. The minimum falls at the same pressure as for C_2, C_3 and C_4; the coil current is lower than for the C curves but is above that for either B_1 or B_2.

The "electromagnetic" theory predicts that the minimum for curves A and B should occur at a pressure of 0.0035 mm for a frequency of 7.2×10^6 cycles per second and at 0.0054 mm for a frequency of 11.0×10^6 cycles per second, the ionizing potential being taken as 10.4 volts. We have found, however, that the dull glow or its equivalent must always be present before the

[9] Here again on running the tube after a change in frequency of the oscillator, the minimum for the first test is displaced with respect to the minima obtained in succeeding tests under otherwise identical operating conditions. In this case however the first minimum is at a higher pressure than the following, corresponding to a change from one frequency to a lower value.

bright glow comes on; we have considered therefore, that the effective ionizing potential is 5.5 volts. The calculated values of the pressure at the minima then become 0.0048 mm for 7.2×10^6 cycles per second and 0.0075 mm for 11.0×10^6 cycles per second; the observed values were 0.0055 mm for curves C at 7.2×10^6 cycles per second, 0.0085 mm for curves A at 11.0×10^6 cycles per second and 0.0065 mm for curves B at the same frequency; the agreement is fair.

The electric theory predicts that the minimum should fall at 0.0031 mm for 7.2×10^6 cycles per second and at 0.0046 mm for 11.0×10^6 cycles per second; the effective ionizing potential of 5.5 volts has been used to calculate these results. The agreement here is much less satisfactory than in the electromagnetic case. Throughout the calculations for the values of the pressures at the minima the mean free path of an electron in mercury vapor at 1 mm of Hg pressure and 25°C has been taken as 0.0149 cm as given by Compton and Langmuir.[10]

The diametral fields set up by the currents in the coil were sufficient to produce ionization but not at the pressures corresponding to the minimum of the bright glow; the mean free path of an electron in mercury vapor is not great enough to permit an electron to acquire sufficient velocity to cause ionization.

One other point in connection with the bright glow curves should be mentioned. Indications are that the furnace temperature, and therefore the bulb and vapor temperature, affects the position of the maximum in the region above 0.05 mm. For temperatures below 170°C, the maxima occur as with curve C_4; for temperatures around 185°C, the curves flatten out as in A_2 and A_3 and for still higher temperatures the curves continue to rise. Further work is in progress in an attempt to determine the relation between the shape of the curve and the furnace temperature.

The curves A_1', A_2' and A_3' were taken simultaneously with the A_1, A_2 and A_3 curves and represent the variation of starting current with pressure for the dull glow corresponding to curves A_1, A_2 and A_3 for the bright glow; the B' and C' curves have a similar interpretation. Curves A_2' and A_3' are entirely above A_2 and A_3; this is a significant fact because an observer could readily have failed to detect the existence of two types of discharge under these conditions. The procedure described above for separating the two components of the discharge was particularly important here; at some value for the current the two discharges appeared simultaneously corresponding to a point on one of the A' curves; the current was reduced until the bright glow disappeared, leaving the dull glow; the current was again increased and the bright glow reappeared at a point on the A curve. A change of inductance from 10.4×10^{-7} henries to 6.84×10^{-7} henries was made in passing from the B' to the A' curves but the frequency was kept at 11.0×10^6 cycles per second. The shift of the curves along the current axis is about twice as great for the dull glow curves as for the bright glow; the change of inductance should have

[10] Compton and Langmuir, Rev. of Mod. Phys. **2**, 208 (1930).

affected them alike. As pointed out above for the bright glow curves the observed ratio of the minimum currents was 0.71 and the computed was 0.89 on the basis of diametral fields; according to the theory the same calculation should hold for the dull glow but the observed ratio is only 0.39. If axial fields are assumed, the computed value for the ratio is 0.99; in either case the observed values for the dull glow fail to fit the theory and the discrepancy is much greater than for the bright glow.

Curves C' were obtained with the same inductance as for curves B' namely 10.4×10^{-7} henries but the frequency was reduced to 7.2×10^{6} cycles per second. On the basis of the electric theory there should have been no change in the values of the minimum currents in passing from B' to C' but actually there were very large changes. Again the shift along the pressure axis is in the wrong direction for the minimum should occur at a lower pressure as the frequency is lowered. Furthermore the currents observed at these minima were not sufficient to set up diametral fields powerful enough to cause ionization; the electrons could not possibly acquire sufficient velocity in the distance equal to the mean free path of an electron in mercury vapor at these pressures. This would seem to indicate that the process is one of multiple collisions.[11]

Curve D' is included to show that even the dull glow curves may be reproduced after a lapse of time although it was much more difficult in general to repeat the dull glow curves than the bright glow curves.

The authors wish to thank Mr. John Mills and Bell Telephone Laboratories for the use of power tubes used in this investigation. They desire, too, to extend their grateful appreciation of the help rendered by Dr. Ann Hepburn in the experimental work.

[11] This is the region of pressures, too, in which the bright glow curves show their change of shape with furnace temperature; it may be possible to explain the change in shape in terms of a variation of the terminal velocity of an electron moving through mercury vapor with the temperature of the vapor, the pressure being fixed by the temperature of the liquid mercury present.

THE PIRANI GAUGE FOR THE MEASUREMENT OF SMALL CHANGES OF PRESSURE

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Abstract

The application of the Pirani gauge to the measurement of small pressure changes is discussed. Both nickel and tungsten wires are used as filaments in the gauge. Nickel wire not only has the greater sensitivity but possesses several other advantages. The theory of the gauge is developed so that it is possible to predict the effect of change in length or diameter of the wire upon the sensitivity of the gauge. The theory also predicts that there is an optimum temperature to which the wire should be heated for maximum sensitivity of the gauge. The observed and computed values of the optimum temperature are compared. In some cases the agreement is as good as can be expected and in the others the discrepancy is easily explained. The maximum sensitivity attained is a galvanometer deflection of 1 mm for a pressure change of air equivalent to 5×10^{-9} mm of mercury.

Introduction

THE possibility of using the variation in heat conductivity of a gas with pressure as a measure of low pressures was first suggested by Pirani.[1] Recent experimenters[2,3] have shown that such a gauge is capable of responding to very small changes in pressure.

These investigators have been primarily interested in a gauge which will determine the actual pressure existing in a chamber after it has been calibrated by comparison with an absolute gauge such as the McLeod. The aim of this experiment is to develop a gauge with a high sensitivity to very small pressure changes.

Theory

It is easily shown that the quantity of heat Q conducted by a gas when the mean free path is large compared to the dimensions of the container is

$$Q = nGAtH/6N \tag{1}$$

where n is the number of molecules per cm^3, G the mean molecular velocity, A the area of the heated element, t the temperature difference between the heated element and its surroundings, H the molecular heat at constant volume, and N the number of molecules per gram molecule. Experimental measurements give a value of the heat transfer which is usually less than that predicted by this equation. This is because the molecules striking the heated wire do not attain temperature equilibrium with it. The ratio of the actual amount of heat conducted from the heated element to that computed by

[1] M. Pirani, Verh. d Deutsch. Phys. Ges. **8**, 24, 686 (1906).
[2] A. M. Skellet, J. O. S. A. and R. S. I. **15**, 56 (1927).
[3] L. F. Stanly, Phys. Soc. Proc. **41**, 194 (1929).

Eq. (1) is known as the accommodation coefficient and has been measured for some gases. Soddy and Berry[4] give the values of the actual amount of heat conducted and the values of the accommodation coefficient for gases striking a heated tungsten surface. The values of the accommodation coefficient range from 0.25 in the case of hydrogen to 1.0 in the case of argon and neon. The values of the actual amount of heat conducted by various gases deviate by less than 10 percent from a mean value for a number of the common gases. Hence we may expect that the sensitivity of the Pirani gauge will be nearly the same for this group of gases.

In the application of the above principle to the measurement of pressure changes the temperature change in the wire resulting from a change in the heat conductivity of the gas is usually measured by the change in resistance. This resistance change is in turn measured by a Wheatstone bridge. If the pressure change to be measured is not large the galvanometer deflection is the most accurate method of determining the magnitude of the change.

The bridge potential serves as a source of power to heat the wire. The energy dissipated by a heated wire must be equal to that supplied, hence neglecting conduction to the leads

$$\frac{E^2}{R} = A\gamma(T^4 - T_0^4) + A\alpha p(T - T_0) \tag{2}$$

where E is the potential across the ends of the wire, R the resistance and A the area of the wire, T and T_0 the temperature of the wire and of its surroundings, respectively, p the pressure of the gas and γ and α constants. Since the resistance change corresponding to the pressure changes normally measured is small we may assume that the power supplied to the wire is constant. Then by differentiation of (2),

$$\frac{dT}{dp} = -\frac{\alpha(T - T_0)}{4\gamma T^3 + \alpha p}.$$

At low pressures the amount of heat dissipated from the wire by radiation is large compared to that conducted by gas hence we may neglect αp in comparison to $4\gamma T^3$. Then

$$\frac{dT}{dp} = K\frac{T - T_0}{T^3} \tag{3}$$

where K is a constant.

Obviously there is a relation between T and T_0 for which the temperature change of the wire will be a maximum for a given pressure change. This relation is given by

$$\frac{d}{dT}\left[\frac{(T - T_0)}{T^3}\right] = 0$$

or

$$T = 3T_0/2.$$

[4] F. Soddy and A. Berry, Proc. Roy. Soc. **83**, 254 (1910).

Substituting this value in (3) we obtain,

$$\left[\frac{dT}{dp}\right]_{\max} = \frac{K'}{T_0^2}. \tag{4}$$

Hence the value of the maximum temperature change of the wire for a given pressure change is inversely proportional to the square of the absolute temperature of the surroundings of the wire.

Since the temperature change resulting from a given pressure change is normally small we may assume that

$$R = R_0[1 + \alpha(T - 273)]$$

or

$$dR = R_0\alpha dT.$$

Substituting this value of dT in (3) we obtain,

$$\frac{dR}{dp} = K''R_0\frac{T - T_0}{T^3}. \tag{5}$$

Obviously dR/dp has the same maximum as dT/dp. The maximum galvanometer deflection does not necessarily correspond to the maximum resistance change, however.

The current through the galvanometer in a Wheatstone bridge circuit is given by

$$I_g = \frac{EdR}{4RR_g + 4R^2}$$

if the battery resistance is small and the four arms of the bridge are approximately equal. Substituting for dR from (5),

$$I_g = K'''\frac{R_0E}{RR_g + R^2}\frac{T - T_0}{T^3}dp. \tag{6}$$

Obviously the galvanometer deflection may be increased by increasing the potential of the bridge. This factor is limited, however, because the wire must be heated to its optimum temperature.

The relation between the potential drop across the wire and the temperature may be obtained from (2). In general the heat conducted by the gas may be neglected in comparison to that dissipated by radiation and T_0^4 in comparison to T^4. Hence

$$E = (\gamma AR)^{1/2}T^2.$$

Substituting this value of E in (6)

$$I_g = K\frac{R_0(AR)^{1/2}}{RR_g + R^2}\frac{T - T_0}{T}dp. \tag{7}$$

The optimum temperature of the gauge wire for maximum galvanometer deflection may be determined from (7). In the general case this solution is difficult but several special cases which are of interest may be treated.

If we assume that the galvanometer resistance is large compared to the resistance of the arms of the bridge, (7) reduces to

$$I_g = K' \frac{T - T_0}{R^{1/2}T} dp.$$

But

$$R = R_0[1 + \alpha(T - 273) + \beta(T - 273)^2]$$

where the terms of second order must be included if the action of the gauge is to be described over any considerable range. Hence

$$I_g = \frac{K'''(T - T_0)}{[1 + \alpha(T - 273) + \beta(T - 273)^2]^{1/2}T} dp.$$

The optimum temperature of the wire may be determined by

$$\frac{d}{dT}\left[\log \frac{T - T_0}{[1 + \alpha(T - 273) + \beta(T - 273)^2]^{1/2}T}\right] = 0$$

or

$$2\beta T^3 + (\alpha - 546\beta - 4\beta T_0)T^2 - T_0(3\alpha - 1638\beta)T - 2T_0[1 - 273\alpha + (273)^2\beta] = 0. \quad (8)$$

If the galvanometer resistance is small as compared to the resistance in the bridge arms Eq. (7) reduces to

$$I_g = K^* \frac{T - T_0}{R^{3/2}T}$$

and the value of T for maximum I_g is given by

$$6\beta T^3 + (3\alpha - 1638\beta - 8\beta T_0)T^2 - 5T_0(\alpha - 546\beta)T - 2T_0[1 - 273\alpha + (273)^2\beta] = 0. \quad (9)$$

Results

The experimental arrangement used in obtaining the results given below is shown in Fig. 1. The leak was controlled by a stopcock so that it could be opened or closed as desired. This gave a constant pressure change and the corresponding galvanometer deflection could be observed for various bridge potentials and various samples of wire.

The gauge formed one arm of a Wheatstone bridge. The other arms consisted of resistances variable in small steps so that the arms of the bridge could be kept approximately equal. The galvanometer used has a resistance of 17 ohms and a sensitivity of 11.6 mm per microvolt. Resistance was connected in series or parallel with it to obtain the high and low galvanometer resistances used.

Equation (7) shows that the galvanometer deflection should be directly proportional to the pressure change. This was verified beyond the limits of the McLeod gauge by connecting a small leak to a pump through a stopcock. This leak was adjusted to give several cm deflection of the galvanometer as

it was turned on or off. As the pressure in the gauge was increased by the use of another leak the deflection produced by opening or closing the first leak remained constant.

Equation (7) also shows that the sensitivity of the gauge is proportional to the square root of the area of the wire. It is possible to multiply the sensitivity of a nickel wire gauge by two or three merely by flattening the wire.

The effect of the length of the gauge wire upon the sensitivity may be determined from (7). Since A, R, and R_0 are all proportional to the length of the wire it is evident that the sensitivity will be directly proportional to

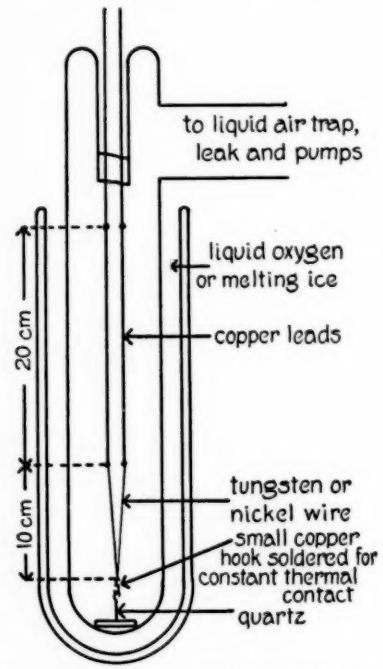

Fig. 1. Construction of the Pirani gauge.

the length of the wire if the galvanometer resistance is large compared to the resistance of the bridge arms. On the other hand, if the galvanometer re-

TABLE I.

Galvanometer resistance	Length of wire (cm)	Maximum deflection
312	20	22.4
	10	12.0
	5	6.3
17	20	23.0
	10	20.1
	5	15.9
3.86	20	24.5
	10	24.8
	5	23.2

sistance is small the sensitivity is independent of the length of the wire. Table I shows the effect of the length of the wire upon the sensitivity of the gauge. In each case the gauge was constructed of nickel wire 0.001 inch in diameter and the walls of the gauge were maintained at the temperature of melting ice.

The variation of the sensitivity of the gauge with diameter of the wire may also be predicted. If the galvanometer resistance is large compared to the resistance of the gauge, the diameter of the wire should be decreased and if the galvanometer resistance is low the diameter of the wire should be increased. Hence for maximum sensitivity the wire should be as long as convenient and the diameter should be adjusted so that its resistance is of the

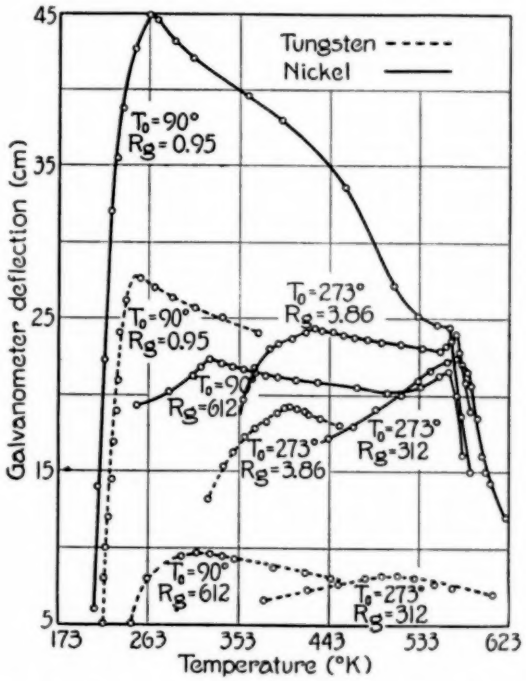

Fig. 2. Curves showing the relation between the temperature of the gauge wire and the sensitivity of the gauge. T_0 is the temperature of the walls of the gauge and R_g the galvanometer resistance.

same order of magnitude as the galvanometer resistance. In general a galvanometer with low resistance is preferable since the corresponding lower resistance in the bridge arms permits the use of lower battery potential which decreases the tendency of the galvanometer to drift.

The relation between the sensitivity of the gauge and the temperature of the wire is shown in Fig. 2. The tungsten and nickel wires used in obtaining these curves were 20 cm long and 0.001 inch in diameter. The temperature was determined by the known relation between the temperature and resistance. For tungsten the values $\alpha = 5.24 \times 10^{-3}$ and $\beta = 0.7 \times 10^{-6}$ were used in the well-known resistance formula. The temperature of the nickel wire

was read from the curve shown in Fig. 3 which was determined for the wire used in this experiment.

It will be noted that all the temperature sensitivity curves for nickel wire (Fig. 2) have either a primary or a secondary maximum at approximately 570°* after which the sensitivity decreases very rapidly. This is obviously due to the rapid increase in the slope of the temperature resistance curve and the sudden break at 615°. The observed temperature at which this break occurs should be less when the wire is used as a gauge because the ends of the gauge wire are cooled by conduction of heat to the leads. This view is substantiated by the fact that the apparent temperature at which the maximum occurs decreases when a shorter wire is used.

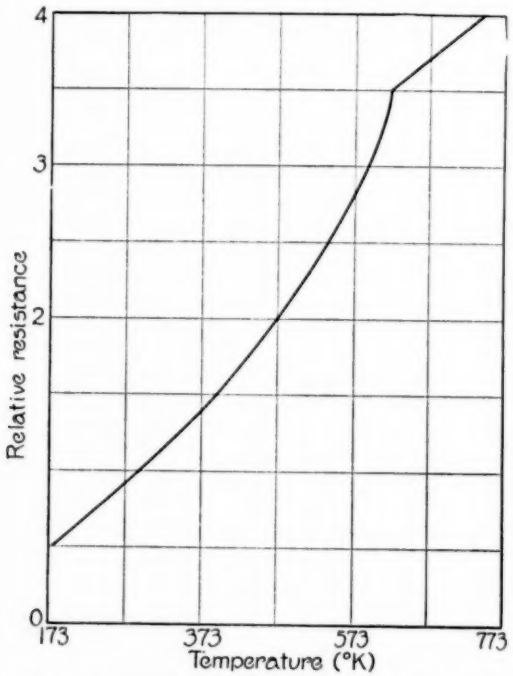

Fig. 3. Temperature resistance curve for nickel wire.

In Table II, T_0 is the temperature of the gauge walls, R_g is the galvanometer resistance, R is the resistance of the wire at its optimum temperature, E is the bridge potential necessary to produce this temperature, T(obs.) and D the optimum temperature and the galvanometer deflection at that temperature, respectively, as determined from Fig. 2, and T (comp.) the optimum temperature computed from Eqs. (8) and (9). In obtaining the values of T (comp.) the proper equation is chosen depending upon the value of the galvanometer resistance, and the values of T_0, α, and β are substituted after which the equation may be solved for T. For tungsten the values of α and β previously given were used and for nickel the same constants were determined from Fig. 3 to fit the curve approximately in the region in which the observed temperature was known to lie. It will be noted that the computed

temperatures when $T_0=90°$ are much lower than the observed. This is partially due to heat conduction along the leads and partially to the decrease in the constant γ appearing in Eq. (2) or, in other words, a decrease in the efficiency of radiation at low temperatures. In fact with a potential of only 0.0003 volt applied to the bridge the lowest temperature attained by the nickel filament was 209° and by the tungsten 213°.

The secondary maxima in the temperature sensitivity curves of nickel wire are not predicted by the equations but they probably would be if the variation in slope of the temperature resistance curve were taken into account and the equation of the curve were expressed more accurately.

TABLE II

	T_0	R_0	R	E	T Comp.	T Obs.	D
Nickel	90	612	41.9	0.5	248	313	22.3
	90	0.95	30.6	0.3	136	261	45.0
	273	312	99.0	2.9	533	563	22.4
	273	3.86	61.8	1.1	429	393	24.5
Tungsten	90	612	23.3	0.5	195	311	9.6
	90	0.95	17.0	0.4	120	254	27.6
	273	312	46.5	3.0	715	513	8.2
	273	3.86	33.5	1.3	415	401	19.3

* All temperatures given on the Kelvin scale.

Table II shows that the sensitivity attained by the use of nickel wire is in all cases greater than that for tungsten. Nickel wire has the additional advantage that it may be flattened more easily than tungsten which greatly increases the sensitivity as the previous discussion has shown. Tungsten wire has the disadvantage that the slightest vibration will cause its resistance to change sufficiently to keep the galvanometer moving back and forth over several cm.

Immersing the walls of the gauge in liquid oxygen approximately multiplies the sensitivity of the gauge by two when the galvanometer resistance is high and by seven when the galvanometer resistance is low. This difference in the sensitivity ratio is to be expected for Table II shows that the resistance of the bridge arms at optimum temperature is much lower when $T_0=90°$ than when $T_0=273°$. Equation (7) and the preceding discussion show that this decrease in resistance will decrease the sensitivity when the galvanometer resistance is high but not when the galvanometer resistance is low.

Many factors enter into the computation of the relative sensitivity of the gauge when the walls are at the temperature of melting ice and at the temperature of liquid oxygen. For example the relation between the pressure and the heat conductivity of the gas will change both because more molecules must be present at liquid oxygen temperatures to exert a given pressure and because the mean molecular velocity is smaller. Also, as previously sug gested, the radiation constant (γ in Eq. (2)) probably decreases at the lower temperature and it is reasonable to expect that the value of the accommodation coefficient depends upon the temperature. The effect of heat conduction

from the filament to the leads upon the sensitivity of the gauge has been neglected so that it is impossible to predict the change in sensitivity which will result from the reversal in the direction of this flow. Such a reversal actually occurs in some cases for when the walls of the gauge are immersed in liquid oxygen the temperature of the filament is less than the temperature of the leads. Due to the impossibility of computing the magnitude of the latter effect and the difficulty in computing some of those previously given no attempt is made to predict the increase in sensitivity when the walls of the gauge are reduced to the temperature of liquid oxygen.

Reducing the walls of the gauge to the temperature of liquid oxygen makes the reaction of the gauge very slow. For example with the gauges at the temperature of melting ice the galvanometer would reach equilibrium about 10 seconds after the stopcock was closed. At liquid oxygen temperature the time required to attain equilibrium was often several minutes. This time lag may be accounted for to some extent by the fact that there must be three times as many molecules in the gauge and their velocity must be much slower when the walls of the gauge are at the temperature of liquid oyxgen so that it should take longer for the gauge to pump out. This factor cannot, however, account for the great difference observed in the time lag in the two cases and neither can it account for the observed fact that the time lag of the gauge decreases rapidly with an increase in temperature of the filament since the area of the filament is so small in comparison to the area of the walls that it can have no appreciable effect upon the mean velocity of the molecules. The observed dependence of the time lag upon the temperature of the wire suggests that it may to some extent be due to the adsorption of a layer of gas by the filament.

It is possible to obtain a galvanometer deflection of 1 mm for a pressure change of air equivalent to $5 \pm 1 \times 10^{-9}$ mm of mercury by forming the gauge from a well-flattened piece of nickel wire 25 cm long and originally 0.0015 inch in diameter and using the galvanometer specified above at maximum sensitivity.

Under similar conditions the sensitivity of the gauge for hydrogen is $4 \pm 1 \times 10^{-9}$ mm of mercury per mm galvanometer deflection.

The sensitivity and characteristics of different gauges will vary due to variations in the original size and the degree of flatness of the wire.

Conclusion

In order to measure pressure changes of less than 10^{-7} mm of mercury it is obvious that the zero position of the galvanometer must be steady. If the ordinary precautions necessary in connecting a Wheatstone bridge of high sensitivity are observed, if the bridge potential is constant, and if the walls of the gauge are maintained at a constant temperature such as melting ice or liquid oxygen, the zero drift of the gauge becomes negligible provided that the pressure changes take place over a short period of time.

The operation of the gauge is not satisfactory when the walls are exposed to the variations of room temperature. A compensating gauge greatly im-

proves the stability of the system but is not as satisfactory as one gauge immersed in a constant temperature bath.

The stability of the gauge may be improved by keeping the bridge potential low. This may be accomplished by proper choice of the galvanometer as previously described and by operating the gauge below its optimum temperature. The extent to which the temperature should be reduced below its optimum value depends upon the difficulty arising from zero drift and upon the rate at which the sensitivity decreases with decrease in temperature. In some cases it is possible to reduce the bridge sensitivity to one half* of its value at the optimum temperature while the gauge sensitivity is reduced only 15 percent. In such cases the decrease in bridge potential would probbably be an advantage.

* That is $\Delta R/R$ for unit galvanometer deflection is doubled.

MEASURING THE INTENSITY OF MOLECULAR BEAMS

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(Received March 20, 1931)

Abstract

A Pirani gauge sensitive to pressure changes of the order of 10^{-8} mm of mercury has been developed and used to measure the intensity of molecular beams defined by two circular openings, one 0.4 and the other 0.6 mm in diameter placed 25 mm apart. The gauge is situated 40 mm from the last opening. A beam of air gives a galvanometer deflection equivalent to 600 cm with a pressure of 0.5 mm of mercury behind the first opening. Under similar conditions H_2 produces a deflection of 1800 cm. The galvanometer sensitivity is 11.6 mm per microvolt. The time lag of the gauge is less than the period of the galvanometer (7 seconds). The limits within which the beam-forming system may be expected to give a Maxwellian distribution of velocities are discussed. The final pressure in the gauge due to a given beam depends upon the dimensions of the gauge opening as kinetic theory predicts. The reduction in intensity of a beam of H_2 by collision with either air or H_2 present in the experimental chamber at various pressures has been measured. The data show that the gauge may be used to measure mean free paths and to obtain more detailed information than has previously been possible as to the probability of scattering through various angles by collision.

Introduction

IN RECENT years the angular distribution of a beam of electrons after scattering by a gas has been studied in detail. No doubt the equally interesting and important problem of the scattering of a beam of molecules or atoms has been neglected because there has not been available a method of measuring the intensity of such beams. The reflection of atoms from a crystal may also be studied advantageously by the aid of a gauge which will measure accurately the intensity of molecular beams. In order to be most efficient in this connection the gauge should have a small internal volume so that it will respond rapidly to changes in beam intensity and small overall dimensions so that it may be placed entirely within the vacuum system and controlled magnetically if this seems desirable. The experiments described in this paper were undertaken to devise such a gauge. Some very notable advances have already been made in this field.[1]

Apparatus

A Pirani gauge, discussed at length in the preceeding paper, was constructed with a small opening in one side (Fig. 1) so that the pressure inside would be affected when the opening was moved into the path of a beam of molecules. By measuring the pressure change inside the gauge a measure of the beam intensity is obtained.

[1] F. Knauer and O. Stern, Zeits. f. Physik **53**, 766 (1929).

The ends of the gauge must be fitted carefully as experience has shown that arrangements which appear to fit well mechanically may leak considerably. The gauge has an internal volume of 0.5 cc so that it responds quickly to changes in beam intensity. The time required for the pressure in the gauge to reach equilibrium is normally less than the period of the galvanometer (7 sec.).

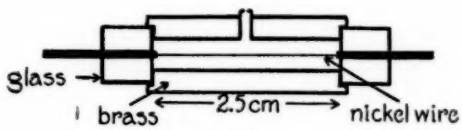

Fig. 1. The Pirani gauge applied to the measurement of molecular beams.

The extreme shortening of the wire seems to have no disadvantage other than decreasing the sensitivity of the gauge. The conduction of heat from the filament to the leads which would, of course, become more troublesome as the length of the filament is decreased has not interfered with the action of the gauge to an appreciable extent.

The apparatus which forms the molecular beam used in the investigation of the characteristics of the gauge consists of 3 circular openings (Fig. 2), the first of which is 0.4 mm in diameter, the second is 0.7 mm in diameter and is situated 1.75 mm from the first, and the third is 0.6 mm in diameter and situated 25 mm from the first. The second opening does not serve to define the beam but merely to prevent the spreading of the comparatively high

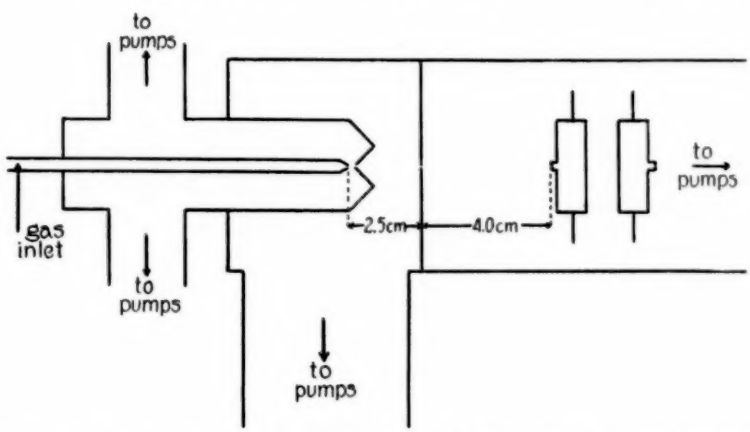

Fig. 2. The construction of the apparatus for the formation of molecular beams.

pressure in B throughout the entire distance between the first and last opening. It is made slightly larger than the other openings in order to eliminate any difficulties there might be in correct alignment. This precaution is hardly necessary here but might be in case very narrow slits were used to form the beam. The third opening was made larger than the first in order to secure a beam in which the width of the maximum intensity portion of the beam would be equal to the diameter of the largest gauge opening used. It is, of

course, obvious that the last opening could be reduced to the size of the first (0.4 mm) thus decreasing the angular divergence of the beam without decreasing its maximum intensity.

The distance between the first two openings of the beam system was adjusted experimentally to give the correct relative pressures in B and C for maximum efficiency. This distance depends upon the relative pumping speeds at B and C which are 4 and 18 liters of air per second, respectively. A change of 0.1 mm in this distance will produce an appreciable reduction in the maximum beam intensity which can be obtained.

A beam system consisting of two openings was not satisfactory for producing beams of high intensity. The impedance inherently existent in an apparatus when two slits are placed near each other makes it difficult to reduce the pressure between them sufficiently for the formation of an intense beam even if the necessary pumping speed is available.

The position of the gauge used in measuring the beam is shown in Fig. 2. It is arranged so that it may be rotated about the last opening of the beam system. The compensating gauge which is placed nearby forms the arm of the bridge adjacent to the main gauge and maintains the bridge balance for general changes in pressure as well as changes in temperature in the experimental chamber. Where high sensitivity is necessary it is advisable to place both gauges in a common metal container or form both from the same piece of metal.

Procedure

The final pressure in the gauge due to a given beam will depend upon the size and shape of the opening into the gauge. The most advantageous form of opening may be predicted by a consideration of Knudsen's law of molecular flow.

Since the pressure in the gauge is always such that the mean free path is large compared to the dimensions of the container, it is evident that the gauge opening, regardless of its length or diameter, will offer no impedance to the entrance of the molecules of the beam if the apparatus is arranged so that they do not strike the walls of the opening. Hence the pressure inside the gauge will build up to such a value that the quantity of gas which flows out through the gauge opening is equal to that which enters it from the beam. The quantity of gas Q measured in cm^3 at 1 bar flowing through a tube of length L and radius r per second is given by Knudsen[2] as

$$Q = \frac{1}{\rho_1^{1/2}} \frac{p_1 - p_2}{W_1 + W_2} \tag{1}$$

where ρ_1 is the density of the gas at 1 bar and at the temperature of the apparatus and the partial impedances W_1 and W_2 are given by

$$W_1 = \frac{(2\pi)^{1/2}}{\pi r^2} \tag{2}$$

and

[2] M. Knudsen, Ann. d. Physik **28**, 75 and **28**, 999 (1909).

$$W_2 = \frac{3L}{4(2\pi)^{1/2}r^3}. \tag{3}$$

Assuming that the molecules emerge from the initial opening of the beam system with a cosine distribution, the amount of gas entering the gauge and also the amount leaving it per second when equilibrium is established is

$$\frac{Q'r^2}{D^2}$$

where Q' is the quantity of gas used in forming the beam, r is the radius of the gauge opening, and D the distance from the initial beam opening to the gauge opening. Substituting the value of Q given above and the values of W_1 and W_2 from Eqs. (2) and (3) in Eq. (1) we obtain upon solving for (p_1-p_2) the quantity actually measured by the gauge

$$p_1 - p_2 \equiv (\rho_1)^{1/2}\frac{Q'}{D^2}\left(\frac{2^{1/2}}{\pi^{1/2}} + \frac{3L}{4(2\pi)^{1/2}r}\right). \tag{4}$$

Hence if the gauge opening is a hole in a thin wall the equilibrium pressure is independent of the radius. If, however, the gauge opening is long as compared to its radius the equilibrium pressure is proportional to its length and inversely proportional to its radius. The effect of the dimensions of the gauge opening upon the sensitivity of the gauge is shown by Table I. The

TABLE I. *The effect of the dimensions of the gauge opening upon the sensitivity of the gauge.*

Dimensions of gauge openings (mm)		Relative deflection	
Length	Diameter	Computed	Observed
12	0.37	18	18
12	0.5	11.3	11.7
12	1.0	6	6.2
4	0.37	6	6
0	0.1	0.6	1

calculated values of the relative sensitivity are obtained from Eq. (4). The agreement is well within the limits to which the dimensions were actually known except in the case of the 0.1 mm hole. Here the disagreement may be explained by the reasonable assumption that the wall has a thickness of 0.08 mm.

For many purposes it is desirable that the molecular beam under consideration have a Maxwellian distribution of velocities. Previous investigators[3,4] have shown that a beam possesses a Maxwellian distribution of velocities if the pressure behind the first opening is such that the mean free path is several times the diameter of the opening and the pressure along the path of the beam is such that the effect of collisions may be neglected. Fig. 3 shows that the latter condition is easily satisfied. As long as the intensity of the beam is proportional to the amount of gas forming it, collisions have not

[3] J. A. Eldridge, Phys. Rev. **30**, 931 (1927).
[4] I. F. Zartman, Phys. Rev. **37**, 383 (1931).

become a factor. Further evidence of the same nature was obtained by plotting beams such as shown in Fig. 4 over a wide range of intensity. In the case of both air and H_2, beams were plotted from the first point shown in Fig. 3 to

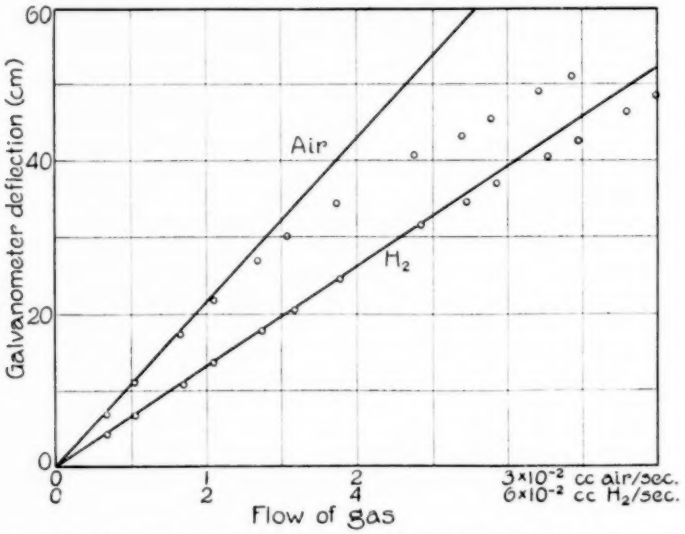

Fig. 3. Volume of gas forming beam plotted against beam intensity. Galvanometer sensitivity, for air 1/10, for H_2 1/20.

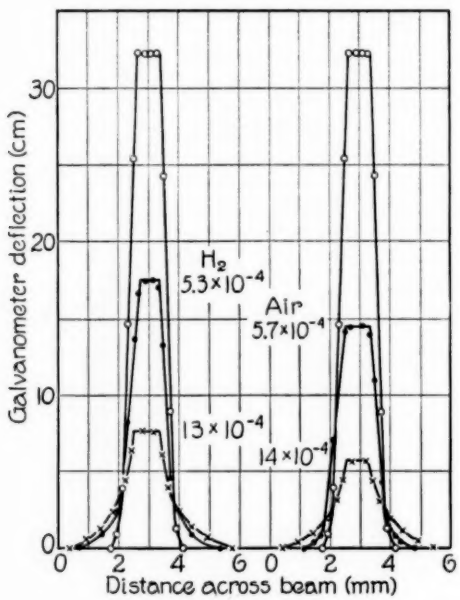

Fig. 4. The spreading of a beam of H_2 with increasing pressures of air and H_2 in its path.

the point where the curves first leave the straight lines. In neither case was there an appreciable spreading of the beam such as would result from collisions taking place between the openings.

The limitation placed upon the beam intensity by the first condition mentioned above may be obtained from Table II. A comparison of the values of the mean free path at A given in this table with the diameter of the opening (0.4 mm) show that the requirement of low pressure behind the first opening, rather than the speed of the pumps, is the limiting factor in the beam intensity which can be obtained if a Maxwellian distribution of velocities is desired. Table II also contains the values of the pressures for the various compartments of the beam system.

TABLE II. *Pressures at various points in the beam system. (mm of mercury).*

	Points from figure 3	A*	B	C	Mean free path at A
Air	1	0.15**	3.2×10^{-4}	1.6×10^{-5}	0.50 mm***
	2	0.26	6.3	3.6	0.30
	4	0.53	13.	3.6	0.14
	8	1.22	27.	3.6	0.07
	12	1.72	38.	3.6	0.05
H_2	1	0.08	2.6×10^{-4}	1.6×10^{-5}	2.0
	2	0.14	4.0	1.6	1.0
	4	0.28	9.0	2.5	0.54
	6	0.42	14	2.5	0 36
	8	0.63	19	3.6	0.24
	11	0.87	28	3.6	0.18
	14	1.08	33	3.6	0.15

The pressure in the experimental chamber is in all cases better than 10^{-6} mm Hg.
* See Fig. 2.
** These values were computed.
*** Mean free path for spherical model assuming air to be composed of oxygen and nitrogen[5].

The equilibrium pressure in the gauge resulting from a given beam may be computed by the application of Eq. (4) and from the calibration constant of the gauge. The comparison of these two values is of interest. The physical constants and the dimensions of the apparatus appearing in Eq. (4) have the following values: $p_1=1.16\times10^{-9}$ (air); $D=6$ cm;[6] $L=1.2$ cm; and $r=0.0185$ cm. The quantity of gas Q' used in forming the beam in the case of the third point on the air curve in Fig. 3 is 8.1×10^{-3} cm^3 at atmospheric pressure or 8.1×10^{3} cm^3 at 1 bar. Substituting these values $p_1-p_2=0.154$ bars or 1.15×10^{-4} mm of mercury. Computing the excess pressure in the gauge from the calibration constant (5.8×10^{-8} mm of mercury per mm galvanometer deflection) and the deflection we obtain $p_1-p_2=1.03\times10^{-4}$ mm of mercury.

The error is approximately 10 percent and is within the limits of accuracy to which the Pirani gauge had been calibrated by comparison with a McLeod gauge.

Similar computations for H_2 yield values of the observed pressures which are approximately 30 percent greater than kinetic theory predicts.

With the aid of a gauge of the type discussed above it should be possible to obtain more detailed information about the nature of molecular collisions.

[5] Dushman, Gen. Elec. Rev. 18, 952, 1042, 1159 (1915).

[6] This value is slightly less than the one given in Fig. 2 because of the increased length of the gauge opening.

The following brief discussion of the decrease in intensity and the scattering of molecular beams by increased pressure in the gauge chamber shows some of the possibilities of the gauge.

The scattering of a beam of H_2 in the experimental chamber is shown in Fig. 4. The beam travels 4 cm in this chamber before striking the gauge opening. In order to eliminate any directional preference of the gauge to the incident molecules a 0.1 mm hole in a thin wall formed the opening into the gauge. This is desirable for as the gauge is turned to one side of the main beam a long opening will permit scattered molecules to enter the gauge with zero impedance only if they are scattered from the portion of the beam which is in line with the gauge opening and at the proper angle to strike that open-

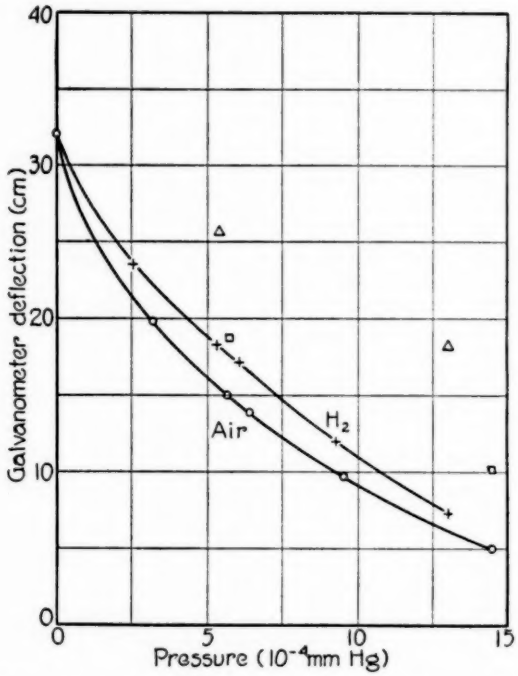

Fig. 5. Beam intensity as a function of the pressure in the experimental chamber.

ing. The hole in the thin wall will, on the other hand, permit the entrance of molecules scattered from any point along the beam. The long opening might be used advantageously for a detailed study of the probability of various scattering angles.

Since the beams shown in Fig. 4 are circular and the readings were taken across a diameter, the actual areas covered by the beams are proportional to the square of the width of the curve.

In Fig. 5 the curves represent the decrease in the maximum intensity of the beams with increasing pressures of air and H_2 in the experimental chamber. The value of the mean free path of H_2 in H_2 as determined from this figure is 3.8 cm at a pressure of 10^{-3} mm of mercury. A comparison of this decrease in maximum intensity and the decrease in the percentage of the

molecules of the original beam which can be found near the center of the beam is of interest. The relative number of molecules found within this limit can be determined by a comparison of the area intensity summations of the curves of Fig. 4. These summations are represented in Fig. 5 by the triangles for H_2 and the squares for air, where the summation of the original beam is represented by 32 and the summations of the scattered beams are relative to the original. For example with an H_2 pressure of 5.3×10^{-4} mm of mercury in the experimental chamber the maximum intensity of the H_2 beam is reduced to 54 percent of its original value while 80 percent of the original number of molecules can be found near the center of the beam. With a slightly higher pressure of air the maximum beam intensity is reduced to 46 percent and 57 percent of the molecules can be found near the center of the beam. This indicates as would be expected that there is greater probability of large angle scattering in air than in H_2.

Conclusion

The only difficulty encountered in the use of these gauges is the elimination of the zero drift. This drift seems to arise principally from unequal evolution of gas from the walls of the beam and compensating gauges, and from changes in room temperature. The latter effect becomes less the more nearly the two gauges are alike but it seems impossible to eliminate it entirely. The drift due to unequal outgassing is, of course, increased with increase in the impedance of the opening. In any case it may be eliminated to a great extent by baking out the gauges so that it is possible to reduce the drift of the galvanometer at maximum sensitivity to one cm in fifteen minutes.

The data given in Fig. 2 and Table II show that a beam of air formed by a pressure of 0.5 mm of mercury behind the first opening of the beam system produces a galvanometer deflection equivalent to 200 cm. H_2 under similiar conditions produces a deflection of 600 cm. Since the above results were obtained, gauges have been constructed with three times the sensitivity of those used in taking the above readings merely by an improved method of flattening the wire and an increase in the length of the wire. Hence we may say that it is possible to form beams of air and H_2 which have approximately a Maxwellian distribution of velocities and produce galvanometer deflections of 600 and 1800 cm, respectively. Allowing a large margin of safety, we may assume that the galvanometer deflections are accurate to 0.5 mm. Then the relative intensity of beams of air may be determined with an accuracy of 0.08 percent. Likewise the intensity of a beam of H_2 may be determined to an accuracy of 0.03 percent. This sensitivity is ample for the determination of the mean free path of gases, for the investigation of the probability of various scattering angles resulting from collision, and for a study of the reflection of atoms from crystals. A scattered beam of H_2 with an intensity of 1 percent of the initial beam may be measured with an accuracy of 3 percent.

LUMINESCENCE DUE TO RADIOACTIVITY

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Abstract

Results of several investigations on luminescence due to radioactivity carried on under the direction of the author are reviewed. It is shown that these results cannot be explained on the well-known active center theory advanced by Rutherford, or any modification of the same such as that proposed by Walsh. In certain substances, including zinc sulphide, there is an initial rise in brightness of the irradiated samples followed by a decay which cannot be represented by a simple exponential curve. It is also found that the rate of decay of brightness is not strictly proportional to the rate of emission of luminous energy as required by the theory. The observed facts can be explained qualitatively by assuming that the alpha, beta and gamma-rays produce excited molecules in the luminescent material. Return of these molecules to their initial state of more stable equilibrium results in emission of luminous energy. The rays also affect the transmission coefficient of the materials, and the apparent decay of brightness is explained as due to the increased absorption of light by the material itself, rather than to the destruction of the hypothetical active centers. This is evidenced also by the fact that in the materials studied, heating the samples usually restores the initial brightness. Quantitative application of these suggestions to the experimental curves was not possible, since the nature of the change in light absorption coefficients resulting from irradiation is not definitely determined.

LUMINESCENCE of certain chemical compounds under the excitation of rays from radioactive substances has been studied by various investigators and theories have been advanced to explain the gradual decay of brightness in these materials.

Rutherford in 1910[1] advanced a theory to explain Marsden's observations on the decay of brightness of phosphorescent zinc sulphide under the action of alpha rays from radon and its decay products. According to his theory, which we shall call the active center theory, phosphorescent zinc sulphide contains initially a number of molecular aggregates known as active centers. Passage of alpha-rays through the compound destroys a number of these active centers resulting in flashes of light known as scintillations. Active centers once destroyed cannot be reformed and since the number of such centers hit by an alpha-ray would be proportional to the number present at any time, the brightness of the compound for a given steady source of radiation should decay in accordance with a simple exponential law.

Chemically pure zinc sulphide does not exhibit this phenomenon to any great extent. The presence of a small quantity of some foreign element such as copper or manganese seems necessary to obtain a maximum effect. This fact lends force to the active center theory since the molecules of foreign matter might act as nuclei for such aggregations.

[1] E. Rutherford, Proc. Roy. Soc. **83A**, 561 (1909–10).

The theory has the virtue of extreme simplicity but none of the subsequent investigators have been able to obtain a simple exponential decay curve of brightness in such compounds, especially when the measurements extended over a considerable period of time. Therefore various modifications have been suggested, from time to time, to make the original theory conform to the observed facts.

Patterson, Walsh and Higgins[2] found that the theory in its simple form did not agree with their measurements of brightness of luminous paints extending over 450 days. There was a distinct slowing up of the rate of decay as time went on, which could be explained if it was assumed that the active centers were capable of recovery in accordance with an exponential law.

In a more recent article Walsh[3] gives additional data on the decay of brightness of luminous paints. The paints consisted of mixtures of zinc sulphide and radium bromide. Measurements of brightness extended over 4000 days.

In this article Walsh, after reviewing various theories advanced on the subject, comes to the conclusion that Rutherford's original theory agrees with his and others' results if the absorption of light by the luminous material itself is taken into consideration.

It is a well-known fact that many transparent substances are colored by the rays from radium. Zinc sulphide used in luminous paints is also colored gradually and its absorption for light progressively increased.

In combining this factor of light absorption with Rutherford's simple theory, Walsh finds, however, that the observed values of brightness agree better with the modified theory if the change in transmission constant of the material due to ionization of inactive centers be put equal to zero; i.e., if the increased absorption be considered as resulting from the destruction of active centers only.

This conclusion can not be justified unless it can be shown that the transmission constant of nonluminescent (inactive) zinc sulphide remains unchanged by the passage through it of ionizing rays. This, however, is not the case. A qualitative test made in this laboratory showed that a film of chemically pure zinc sulphide, exposed to alpha-rays from radium for a short time, is distinctly colored with resulting increase in absorption constant, although practically nonluminescent. Therefore even if in a luminescent compound the ratio of inactive molecules to active ones may be considered small at the start, evidently this ratio is constantly increasing due to the transformation of active molecules to inactive ones as required by the theory. And since these undergo a similar change in transmission constant, their effect on the decay of brightness cannot be neglected in the final analysis.

A number of researches on luminescence due to radio-activity have been carried on in this laboratory. An attempt to explain the results of these observations on the active center theory, with such modifications as have been suggested, was unsuccessful.

[2] Patterson, Walsh and Higgins, Proc. Phys. Soc. Lond. **19,** 215 (1916–7).

[3] J. T. Walsh, Proc. Phys. Soc. Lond. **39,** 318 (1926–27).

Karrer and Kabakjian[4] showed that mixtures of radium bromide and barium bromide acquired the property of luminescing with an intense bluish light by simply heating the compounds to a suitable temperature and then cooling. The luminescence decayed in time but could be completely regenerated by heating the compound to the original temperature. Addition of foreign substances was not necessary in this case. In fact addition of minute quantities of copper or manganese seemed to reduce the brightness.

Rodman[5] investigated the decay of brightness of pure radium bromide, and also of some mixtures of radium bromide and barium bromide. Two points were brought out in her paper. First that the decay of brightness did not conform to a simple exponential law. Second, that although the decay was very rapid at the start, the curve representing the brightness became finally parallel to the time axis, giving a constant value of brightness which was not zero. Both of these facts are at variance with the active center theory.

For example, the brightness of pure radium bromide decayed to about one percent of its initial value in 24 hours. It reached a constant value in about 300 hours and did not show a measurable variation in the following 200 hours.

Smith[6] investigated the luminescence of pure barium bromide exposed to alpha, beta and gamma-rays. In his case the source of the rays and the luminescent material were kept separate so that it was possible to observe the variation of brightness from the start. Smith's results showed an initial rise in brightness of barium bromide on exposure to the rays from radium. This rise continued for several hours reaching a maximum value and then decaying to a final constant value.

It is quite evident that Smith's results cannot be explained by the active center theory which fails to account for the initial rise in brightness. The final approach of brightness to a constant value instead of zero is also in agreement with Rodman's results.

Since the original active center theory was formulated by Rutherford to explain the decay of luminescence in zinc sulphide, it was considered desirable to investigate this compound by a similar method.

Gessner[7] undertook this investigation by means of an improved type of apparatus. The constant source of rays was well separated from the luminescent material and the apparatus so arranged that readings of brightness could be taken within two minutes after the exposure.

The results obtained by Gessner were similar to those of Smith. In every case there was an initial rise in brightness, followed by a decay which was not exponential. Neither did any part of the curves conform to the modified theory developed by Walsh.

This initial rise in brightness of zinc sulphide was also observed by Marsden for beta-ray excitation, but no attempt was made to explain this fact in formulating the active center theory.

[4] E. Karrer and D. H. Kabakjian, Jour. Frank. Inst. **186,** 317 (1918).
[5] J. Rodman, Phys. Rev. **23,** 478 (1924).
[6] L. E. Smith, Phys. Rev. **28,** 431 (1926).
[7] G. S. Gessner, Phys. Rev. **36,** 207 (1930).

Since the alpha-rays produce individual scintillations, while the beta-rays produce more or less diffuse illumination, it may be assumed that the mechanism of light emission is different for the two rays. Chariton and Lea[8] have found, however, that scintillations similar to those produced by alpha-rays can be obtained from beta-rays under favorable conditions, showing clearly that the only difference between the two types of excitations is the energy carried by the individual rays.

That the rise observed in Gessner's samples was not due to beta-rays was evidenced by the fact that a polonium plate used to excite the compound gave the same type of brightness curve.

In attempting to check Walsh's latest explanation on the decay of zinc sulphide paints, Gessner had used thin films of zinc sulphide and a more intense source of radiation, hoping thereby to accelerate the rate of decay. The brightness of his samples were uniformly greater than those of Walsh. If the emission of light results from destruction of active centers, evidently these

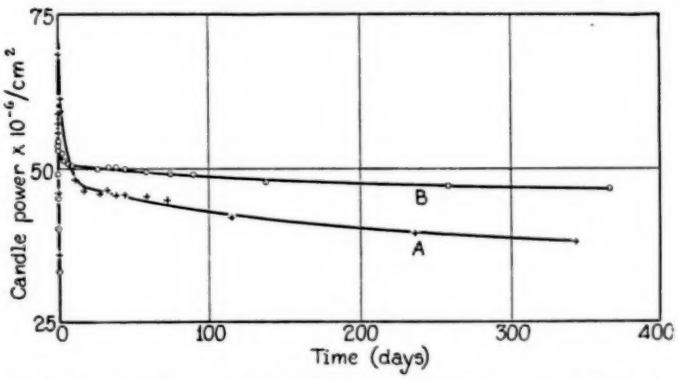

Fig. 1. Curves showing the decay of brightness in zinc sulphide. *A*, alpha, beta and gamma-rays from radium. *B*, beta and gamma-rays. Thickness of material, 0.022 cm.

were being destroyed at a greater rate, and since the volume of the material used, and presumably the initial number of active centers was very small, one would expect the brightness of these samples to decay much faster than those of Walsh. The results were quite the opposite. Walsh's brightest sample (Sample *H*, initial brightness 0.28 candles per square meter) shows a decay of over 85 percent in 400 days whereas one of Gessner's samples (Sample 4, Maximum brightness 0.4 candles per square meter) shows a decay of less than 50 percent for the same interval. This disagreement with the theory can hardly be explained by possible differences in the materials used by the two investigators.

It was also found that in the same material of approximately the same thickness the rate of decay was not in direct proportion to the rate of emission of light but depended on the nature of exiciting rays.

Fig. 1* illustrates this point. Although the total amount of light emitted

[8] J. Chariton and C. A. Lea, Proc. Roy. Soc. **A122,** 335 (1929).

* Curves represented in Fig. 1 and Fig. 2 were obtained by Mr. Gessner. For apparatus and the method of measurement, refer to his article, Phys. Rev. **36,** 207 (1930).

by sample B, due chiefly to beta-ray excitation is greater than that from sample A where alpha-ray excitation predominates, the rate of decay of brightness is in the reverse order. Assuming that the mechanism of light emission is the same for the two types of radiation this difference in the rates of decay of the two samples cannot be explained on the active center theory.

Another check on the theory could be obtained by estimating the number of active centers in zinc sulphide from the data given in Fig. 1, on the assumptions made by Walsh in estimating the number of active centers in his samples.

By integrating the area under curve A, the total amount of luminous flux produced in a quantity of zinc sulphide having a thickness of 0.022 cm and an area of one square cm can be computed from the formula

$$F = \frac{4\pi aI}{1 - e^{-0.022a}}$$

where F is flux in lumens; I is brightness in candles/cm^2; and a is the coefficient of absorption of freshly prepared zinc sulphide.

Taking the value of a as 32 and the mechanical equivalent of light for the wave-length emitted as 660 lumens per watt, the amount of luminous energy radiated by this sample during the first 350 days is roughly equal to 1.5×10^{10} ergs.

If N is the number of active centers destroyed during this interval of time and if it be assumed that each active center emits, on destruction, one quantum of energy corresponding to a wave-length of 550mμ, the total amount of energy radiated by the destruction of N active centers will be equal to $N\cdot3\cdot6\times10^{-12}$ ergs. Equating this with the above expression we have

$$N = \frac{1\cdot5\times10^{10}}{3\cdot6\times10^{-12}} = 4.16\times10^{21}.$$

But the number of molecules in this quantity of zinc sulphide is approximately 5.5×10^{20}. Therefore the number of active centers destroyed in this sample during the first 350 days comes out more than 7 times the number of molecules present. Since the brightness of the sample has decayed to 56 percent of its maximum value and the rate of decay has become very much slower it must be assumed that the original number of active centers present is many times the number of molecules present in the material if the active centers once destroyed cannot be regenerated.

The active center theory of luminescence, therefore, seems inadequate to explain, among other things:

(1) The initial rise in brightness of all the samples investigated;

(2) The difference in the rate of decay of brightness in luminescent material for alpha and beta-ray excitations;

(3) The general nature of brightness decay curves.

In view of these facts it seems more reasonable to assume that the passage of the rays through luminescent materials results, not in destruction of any hypothetical active centers, but rather in producing excited molecules which emit light on returning to their normal energy levels. As this is a reversible change this phenomenon can continue indefinitely.

The rays may also produce a certain amount of ionization or dissociation resulting in a more stable change such as coloration, due to the inability of the ions to recombine at ordinary room temperatures. The two phenomena are not strictly interdependent. It is possible to have coloration with very little luminescence and vice versa.

Light emission by excited molecules can take place in two distinct ways, giving rise to two types of luminescence. If the whole absorbed energy is re-emitted instantaneously, unaffected by the temperature of the absorbing material, the phenomenon is known as fluorescence. If, however, the absorbed energy is re-emitted gradually and the absorption and emission are more or less dependent on the temperature of the absorbing material, the phenomenon is known as phosphorescence. What is known as thermoluminescence is really phosphorescence at higher temperatures.

In this paper the term phosphorescence is used in a general sense without regard to the nature of the exciting rays. Its characteristic feature is the inability of the excited molecules to return at once to their normal state, consequently a phosphorescent material will continue emitting light after the exciting rays have been removed.

If the luminescence produced by alpha, beta and gamma-rays in the investigated materials is of the phosphorescent type, the initial rise in brightness of these samples could be explained. This would mean that all the energy absorbed from the rays is not radiated at once. It can be shown that this is generally true for the materials under discussion. Even in the case of alpha-ray excitation of zinc sulphide a diffuse radiation lasting several minutes follows each scintillation. This can easily be demonstrated by exposing a zinc sulphide screen to a strong source of alpha-rays for a few seconds. When the source is removed the screen will continue to glow in the dark for several minutes, its brightness gradually decaying to zero. It can also be shown that this is due to slow radiation of the energy absorbed from the alpha-rays and not to a possible absorption of its own luminous energy.

At ordinary room temperatures the ratio of energy radiated as diffuse light to that radiated as scintillations is small and has usually been overlooked, but this ratio is dependent on the temperature of the absorbing material. If a zinc sulphide screen in contact with a polonium plate is cooled to the temperature of liquid air its brightness is considerably diminished. When after a few minutes of exposure the polonium plate is removed and the screen is allowed to reach the room temperature, it glows much more brightly, showing that a larger percentage of the energy of the rays is absorbed and retained at the lower temperatures and released only with the aid of heat agitation of the molecules.

These experiments justify us in regarding the absorption and emission of

energy by luminescent materials when excited by alpha, beta and gamma-rays, as essentially a phosphorescence phenomenon. If this view is correct then the brightness of these materials, when excited by a constant source of rays should rise to a maximum where the rate of absorption and emission balance each other, and if there is no physical or chemical change in the material, it should remain constant at this value indefinitely. But it is well known that the coefficient of light absorption of these materials increases as a result of irradiation, therefore the brightness must decay in time, not necessarily because of a decrease in the amount of light produced but due to the fact that more and more of it is absorbed by the material itself as time progresses.

Again if the coefficient of absorption never becomes infinite but tends to approach a constant as time approaches infinity, the brightness would never decay to zero.

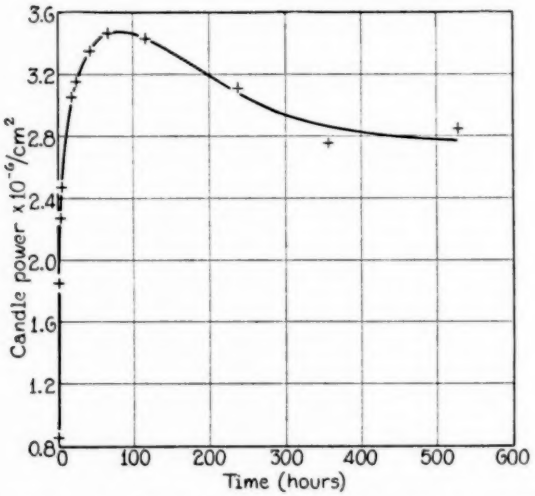

Fig. 2. Luminosity curve. Capsule *A*, beta, gamma-rays. Calcium sulphate Mn activated.

These conclusions are qualitatively in agreement with the observed facts on all materials investigated in this laboratory.

Fig. 2 represents the rise and decay in brightness of a typical thermoluminescent material which is also phosphorescent at ordinary room temperatures. The material consists of crystalline calcium sulphate activated by manganese. It will be noted that the brightness increases in time reaching a maximum in about 70 hours and then begins to decay. The decay curve is not a pure exponential and final brightness will never become zero. The similarity between the characteristics of this curve and those obtained by Smith and Gessner is quite apparent.

The factor controlling the decay of brightness seems to be the change in the transmission constant of the material. In pure barium bromide this change is small and its rate of decay is also small. The final constant value of brightness for samples investigated by Smith varied from 40 percent to 60 percent of their maximum. On the other hand in pure radium bromide, which becomes

almost black, the rate of decay is very large and the final constant value of brightness is about 0.1 percent of its maximum. Both radium bromide and barium bromide completely recover their maximum brightness on heating to an adequate temperature. The heating results also in complete disappearance of any coloration.

According to this view luminous paints which have decayed should also regain their brightness if the coloration of the crystals is removed. This was attempted on some samples of zinc sulphide paints which had been allowed to decay for over eleven years in sealed tubes. The paints contained 50 and 100 micrograms of radium element, respectively, per gm of zinc sulphide. On heating the tubes over a bunsen burner the brightness was promptly restored but the degree of restoration could not be determined since no record of the initial brightness of the paint was available. The coloration of the samples disappeared at the same time and their photosensitiveness was also revived.

It is not claimed here that there is no chemical decomposition in the irradiated samples resulting in a decrease of light emission. But it has been shown that an attempt to explain the decay of luminescence as due to disappearance of active centers gives inconsistent results, and since it has been shown that the change in transmission constant plays such an important part in the apparent decay of brightness, a quantitative application of any theory of luminescence becomes difficult until the exact nature of this change is determined experimentally.

It has already been shown that the increase in absorption constant cannot be considered as due to the destruction of hypothetical active centers. On the other hand the curves representing the rise and decay of brightness do not furnish sufficient data to determine the nature of this change. Experiments are under way to determine directly the variation in the transmission constant of some of these materials as a result of irradiation, when a quantitative application of the assumptions made above to the experimental curves will become possible.

If the absorption coefficient a is defined by the expression $I_x/I = e^{-ax}$ where I_x/I is the fraction of light transmitted through thickness x of the absorbing material, it is quite evident that a is a variable quantity in this case, its value depending upon the nature and intensity of the radiation and the time.

$$a = f(R, t).$$

In correcting for the absorption of light by the walls of the glass containers Walsh assumes a transmission factor, due to the coloration of glass, of the form

$$T = e^{-pt}$$

where p is a constant for a given tube and t is the time. This is based on the assumption that the coloration of the glass is produced by the destruction of certain molecules in the glass. On this view the transmission should become zero when t is put equal to infinity. If, however, the coloration of transparent materials is due to ionization of the molecules, such ionization might have a

saturation value, in which case the transmission factor would be represented by an expression of the form

$$T = a \cdot e^{-\beta(1-e^{-ct})}$$

where a, b and c are constants for a given material and a given intensity of radiation of one type. In this expression the value of T is never equal to zero. This is more in accordance with the experimental facts. However this may prove to be, it has been shown that experimental results recounted in this paper cannot be satisfactorily explained on the active center theory of luminescence without further modification.

The writer wishes to acknowledge his indebtedness to Mr. Gessner for the use of data obtained by him and to Dr. H. C. Richards and Dr. E. E. Witmer for many valuable suggestions and criticisms during the preparation of this paper.

THE ELECTRIC FIELD, ATMOSPHERE AND EFFECTIVE TEMPERATURE OF THE SUN

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Abstract

The study of important electromagnetic effects in the solar atmosphere undertaken in previous papers is continued. It is shown that the large observed spread of effective temperatures of the sun's radiation can be accounted for by the presence of electric and magnetic fields in the solar atmosphere. The magnitude of the electric field at a level where the magnetic field is 25 gauss, calculated from the observed spread of temperatures, is found to be 0.015 volts.cm and agrees well with 0.013 volts/cm calculated earlier from the observed anomalous motions of the solar atmosphere. Gravitational equilibrium is found to be unnecessary in all regions of the atmosphere and it is shown that the "support" and stability of the chromosphere and its anomalous eastward motion are evidences of precisely the same electromagnetic mechanism. An electric field of the value given above is shown to account qualitatively for certain bright line spectra in the chromosphere of the sun. The strange observed relation between bright line spectra and rapid axial rotation of stars, just pointed out by O. Struve of the Yerkes Observatory, confirms in a striking manner some of the conclusions of this and earlier papers.

IN A series of papers it has been shown that the anomalies of the solar rotation arise from electromagnetic effects which take place in the crossed electric and magnetic fields existing in the ionized solar atmosphere. The magnitude and direction of the magnetic field is readily determined by observation, but the magnitude of the electric field is much too small to produce measurable Stark effects and must be inferred from the observed atmospheric motions. In the present paper we consider a method of calculating the magnitude of the electric field from spectroscopic data and will show that the departures of the solar radiation from that of black-body radiation lead to a value for the electric field which agrees with that calculated in earlier papers. Measurements show that the effective solar temperature calculated from the quality of solar radiation is over 1000° higher than that inferred from measurements of the density of radiation. The difference of the effective temperatures is so great that we must conclude that processes other than thermal must be present which add energy to the ions. It is clear that an electric field of sufficient magnitude might add energy to the ions during their free path so that on collision they would have energies higher than that indicated by the temperature of the region. A rough calculation shows that a radial electric field alone will not account for the observed features of the solar radiation, for if there were no solar magnetic field the conductivity of the atmosphere would be so great that electric fields would be very small. However, if we consider both electric and magnetic fields the difference in the effective temperatures is readily accounted for.

Effect of Crossed Electric and Magnetic Fields

In earlier papers[1] we considered the effect of crossed electric and magnetic fields on the electrical conductivity, diamagnetism and mass motion of an ionized gas. It has been shown[1] that diamagnetism limits the solar magnetic field and the resulting distribution is such that the field is nearly tangential to the surface over most of the sun. The electric field, by symmetry, must be radial so that in the following we may assume for simplicity that the electric and magnetic fields are always perpendicular.

The path described by an ion in perpendicular electric and magnetic fields is a cycloid.[2] An ion starting from rest is initially acted upon only by the electric field which accelerates the ion; as the velocity increases the magnetic force at right angles to its motion increases until the ion is moving at right angles to the electric field. The magnetic force continues to act and the ion is forced by its inertia to move against the electric field, whereby it loses energy till it comes to rest. The process then repeats itself again and again. The net result of this process is that the ion progresses in a direction perpendicular to both the electric and magnetic fields and on the average does not advance in the direction of the electric field.

It is clear that in certain parts of the cycloidal path the ion has much more energy than at other points, and if the ion collides at a point in its path where its energy is large, ionizing effects will be greater than if the ion collided in a part of the path where the energy is small. In the general case the ion starts its path with a certain thermal energy and in tracing its cycloidal path it acquires and loses energy repeatedly from the electric field. If R is the radius of the generating circle of the cycloidal path, E the average electric field encountered by the ion in its path, and e the ionic charge in e.m.u., then the difference in energy W of the ion between the top and bottom of its path is

$$W = 2REe. \tag{1}$$

This energy is obviously supplied by the electric rather than the magnetic field, for the motion of the ion is always at right angles to the magnetic force and hence the magnetic field cannot transfer energy to the ion or the ion energy to the magnetic field. It is of importance to note that Eq. (1) gives the maximum energy difference and no matter how long the free path, the ion cannot acquire more. We neglect the less frequent case of successive collisions where an ion of initially large energy collides with another at a favorable point in its path and this ion in turn picks up additional energy and passes it on to still another.

The radius of the cycloidal generating circle R is given by

$$R = \frac{mv}{Be}\left[1 - \frac{2u}{v}\cos\delta + \frac{u^2}{v^2}\right]^{1/2} \tag{2}$$

where m is the mass of the ion, v the initial ionic velocity in a plane perpen-

[1] R. Gunn, Phys. Rev. **32,** 133 (1928); **33,** 614 (1929); **33,** 832 (1929); **34,** 335, 1621 (1929); **35,** 635 (1930); **36,** 1251 (1930); **37,** 283 (1931).

[2] L. Page, Phys. Rev. **33,** 557 (1929).

dicular to the magnetic field B, u the ion drift velocity resulting from the crossed electric and magnetic fields and δ the angle between u and v. When the free paths are long and the electric and magnetic fields are perpendicular, u is given by

$$u = E/B. \tag{3}$$

A few of the ions will acquire and expend the maximum energy given by Eq. (1) and some will lose energy. To get the mean gain in energy for a typical ion we will simply take an arithmetical average and therefore we have from Eqs. (1), (2), and (3) that

$$W_1 = mvu\left(1 + \frac{u^2}{v^2}\right)^{1/2} = \frac{E}{B}\left[2mkT\left(1 + \frac{mE^2}{2kTB^2}\right)\right]^{1/2} \tag{4}$$

where W_1 is the approximate mean increase in energy and $(2\,mkT)^{1/2}$ has been written for mv. The mean increase in energy W_1 may, for convenience, be expressed in terms of an equivalent effective temperature and be equated to $3k\Delta T/2$ where k is the Boltzmann constant and ΔT is the change in effective temperature due to electrical effects. Making this substitution and transforming Eq. (4) we have

$$\frac{\Delta T}{T} = \frac{2u}{3}\left[\frac{2m}{kT}\left(1 + \frac{mu^2}{2kT}\right)\right]^{1/2} \tag{5}$$

or if we solve this for the electric field E we have

$$u^2 = \frac{E^2}{B^2} = \frac{kT}{m}\left[\left(1 + \frac{9}{4}\left(\frac{\Delta T}{T}\right)^2\right)^{1/2} - 1\right]. \tag{6}$$

In Eq. (5) we note that the difference in the effective temperatures is proportional to the square root of the ion mass. This indicates that the ions rather than the electrons are the particles effective in increasing the apparent temperature of the solar atmosphere although there is no reason why the ions cannot transfer their high energies to electrons by collision.

Departure from Black-Body Radiation

Several writers[3,4,5,6] have studied the solar radiation and found it to depart markedly from a black body distribution. At one time it was thought the departures were due to varying general absorption in the radiating layers but Milne[4] concluded that this was quite inadequate. Eddington[6] has reworked some of the data and gives 4660° for the effective temperature of the sun as calculated from the density of radiation and 5740° as the effective temperature calculated from the quality of the radiation. It is clear that the emitted light is much richer in high frequency radiation than would be the case if the sun radiated like a black body. The differences in the effective temperatures, or 1080°, is so great that the energies of some of the ions must be considerably more than that of the mean value. If we are not particularly

[3] C. G. Abbot, Annals Astrophys. Observ. Smithsonian Inst.
[4] E. A. Milne, Monthly Notices **81**, 375 (1921).
[5] Lundblad, Nova Acta, Reg. Soc. Sci. Upsalienses **6**, #1 (1923).
[6] Eddington, Internal Constitution of the Stars.

concerned with the detailed mechanism of the radiation process, Eq. (5) of the preceding section permits a test of our prediction that the effects arise from an electric field in the solar atmosphere. Earlier work[1] showed that the mean atomic weight of the solar atmosphere in the region of the reversing layer was 6.6 if no account were taken of the electrons, or calling the mass of the hydrogen atom h, the mean mass of the ions in the reversing layer is 6.6 h. Moreover, the superposed atmospheric drift velocity u is known from astronomical data to approximate 0.5 km/sec. Substituting in Eq. (5), $m=6.6h$; $h=1.64\times10^{-24}$ gm; $u=5\times10^{4}$ cm/sec; $k=1.37\times10^{-16}$ and $T=4660°$ we find $\Delta T/T=0.197$ so that $\Delta T=920°$. This value is to be compared with the observed value 1080° and is considered satisfactory because the method of averaging to get statistical values is rough. The agreement is greatly improved if we select a mean value for the effective temperature rather than the lower value derived from the density of the solar radiation. Observation shows that the superposed drift velocity u does not change rapidly with altitude in regions which can be observed so that according to Eq. (5), ΔT also changes but little with altitude. This is consistent with the observed fact that the intensity-frequency curve decreases very rapidly on the high frequency side of the maximum. Our calculations clearly indicate that the observed spread of effective temperatures can be accounted for by the presence of electric and magnetic fields in the solar atmosphere.

Magnitude of the Electric Field

In other papers[1] the relation of the mechanical motions of the solar atmosphere to electromagnetic effects was considered and it was concluded that the observed motions required that the solar atmosphere have an electric field directed radially inward and amounting to 0.013 volts/cm in the region where the magnetic field was 25 gauss. The magnitude of the electric field cannot be checked by Stark effect observations and it becomes necessary to look elsewhere for supporting evidence. The spread of observed effective temperatures provides an independent method of calculating the magnitude of the field and we turn at once to Eq. (6) which connects observed quantities with the electric field. We follow earlier work and take $m=6.6h$; $h=1.64\times10^{-24}$ gm; $k=1.37\times10^{-16}$; $T=4660°$; $\Delta T=1080°$ and $B=25$ gauss. Substitution in Eq. (6) gives $E=0.0148$ volts/cm. The agreement of this value with the earlier calculation[1] is most satisfactory and it is evident from the form of Eq. (6) that the agreement will be equally satisfactory at all other levels of the solar atmosphere. The present method of calculating the field is apparently incapable of determining the sign of the electric field, but, as we have pointed out previously, the sign inferred from the solar motions is precisely the sign observed on the earth, i.e., negative or radially inward. The agreement of the two methods of calculating the magnitude of the field strongly supports the conclusion that a solar electric field exists and that the mass motions of the atmosphere and the differences observed in the effective solar temperatures are simply different aspects of the same fundamental physical phenomena.

Stability of the Solar Atmosphere

Eclipse spectra show that large amounts of material, notably calcium, exist high in the chromosphere and the distribution of this material is such that it cannot well be in gravitational equilibrium with a supporting gaseous pressure. Milne[7] has attempted to account for the support and stability of this material by assuming that radiation pressure was great enough to overcome the gravitational forces. His calculations show that the calcium must absorb selectively in what appears to be a highly artificial manner. A still more serious objection to his theory is the fact that once sufficient absorption is built up by special assumptions the atom will be blown away from the sun because the radiation pressure does not decrease as rapidly as gravity. Thus Milne's atmosphere is unstable.[6]

Our study of electromagnetic effects suggests that the stability of the chromosphere does not depend on a specialized type of dance on a sunbeam but does depend on very real and sufficiently large electric and magnetic forces. Although the force on a positive ion in the solar atmosphere is vertically downward and hence in the same direction as gravity, we have seen that the ion does not move downward but on the average moves parallel to the solar surface. Thus ions executing long free paths in crossed magnetic and electric or gravitational fields are "supported" and can progress in the direction of the force field only by numerous collisions. It is therefore clear that it is not necessary to think of the very long free path ions in the solar atmosphere as being in gravitational equilibrium. To illustrate, suppose that neutral molecules of all materials are shot, undeviated by the magnetic or electric fields, by thermal processes to high altitude regions of low pressure where they immediately become ionized. The recombination coefficient will be different for different kinds of ions and those particles that remain neutral for an appreciable time will be acted on by gravity and drop to lower levels. The ions with very small recombination coefficients (calcium for example) will spend most of their life in an ionized condition and therefore will be "supported" and at the same time swept parallel to the solar surface with a velocity dependent on the ratio of the crossed electric and magnetic fields. Eventually an equilibrium condition will be reached and the supply of neutral calcium atoms will balance the loss of those dragged down by the electric field as the result of a large number of collisions and the few which are neutralized and fall under the action of gravity. We thus see that no special mechanism is necessary to account for the "support" of the chromosphere and that it is supported by precisely the same mechanism that produces its observed anomalous eastward drift.

Bright Line Spectra

Doubly reversed, or bright line spectra, are characteristic of certain types of stars but there have been theoretical difficulties in accounting for their presence. Eddington[6] has reviewed the subject and he concluded without attempting to make the statements quantitative, "that bright lines in the spectrum of a static star indicate that either (a) the star is greatly disturbed

[7] E. A. Milne, Monthly Notices **84,** 354 (1924).

by "thunderstorms" or (b) it is a nebulous star." The sun can hardly be called a nebulous star and we should be able to account for certain lines of the flash spectrum by electrical excitation of the type we have considered. The electrical field will add considerable energy only to an ionized particle and more analysis will be necessary to determine the exact mechanism by which an atom is excited to radiation. In another place we have expressed the ratio of the energy added to an ion, to its thermal energy in terms of temperatures and, as a numerical example, we will calculate the ratio of the energies for a helium ion. In Eq. (5) we will take $m = 6.56 \times 10^{-24}$ gm; $u = 5 \times 10^4$ cm/sec; $T = 4660°$ and we find $\Delta T/T = 0.16$; that is to say, all the helium ions periodically acquire energies 16 percent greater than their thermal energies. Similarly the added energy for calcium is 50 percent while that of hydrogen is only 8 percent. Thus we are led to believe that the additional energy available is adequate to produce bright line spectra. For the purpose of this paper, which is primarily concerned with the solar electric field, the rough value given above is adequate, but it is evident that a complete study of the bearing of an electric field on the ionization equilibrium relations in stars is necessary to give a complete description of the events. Saha's[8] theory of stellar ionization will be readjusted to take account of the fields and it is expected that such a readjustment will improve the agreement of his formula with observation.

Conclusion

We have indicated in outline that spectroscopic data regarding the sun bear out our earlier conclusion that electromagnetic phenomena are important in the solar atmosphere. It is rather surprising that the apparent solar rotation should be so closely related to the spectral distribution of radiation from the sun but we have had a suggestion that this might be true in a recent paper by Struve.[9] Dr. Struve has noticed a remarkable correlation between the rotation of stars and their spectral class. The early type stars rotate with great rapidity and several are apparently on the verge of rotational instability. The considerations of the present paper indicate that the early type stars have electric and magnetic fields of considerable magnitude and that our sun is probably a fair representative of stellar bodies. A complete study of the sun is therefore of the greatest importance if we are to understand and correctly interpret the physical phenomena which astronomers observe.

Note added March 24, 1931:

The March issue of the Astrophysical Journal has just appeared and contains another paper by O. Struve giving observational data which is in remarkable accord with the theory developed above. Dr. Struve states "Excessive rotations, estimated at 9 or 10 (. . . 250 km/sec.), are frequent. Apparently bright lines occur preferentially in stars having rapid axial rotation."

The relation of Eq. (5) shows that the ratio of the additional excitation energy to the thermal energy is directly proportional to the superposed drift velocity u. Thus theory predicts a strict parallelism between high *apparent* rotations and bright line spectra. Struve's results appear to be a beautiful confirmation of the material of this and preceding papers.

[8] M. N. Saha, Phil. Mag. **40**, 472, 809 (1920).

[9] O. Struve, Astrophys. J. **72**, 1 (1930).

MOLECULAR ASSOCIATION

By J. Albert Wehrle
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(Received March 20, 1931).

Abstract

To study the molecular association of nitrobenzene, the dielectric constant of mixtures of this substance with benzene (nonpolar solvent) and polar liquids (ethyl ether, chlorobenzene and acetone) was measured. The molar polarizations of the two polar substances were calculated as a function of the concentrations. If the dependence of the molar polarization of one polar liquid on the concentration of the other is taken as a measure of the association, the experiments show that the larger the electric moment of the molecule, the stronger is the association. They also show that association takes place not only between the molecules of a given substance, but also between two substances that may be quite different, provided they are both polar.

Introduction

THE polar liquids or gases, i.e., those whose molecules have an electric moment, show some deviation from simple additive or linear laws at certain concentrations. The explanation for these deviations is that the molecules associate, i.e., form complexes bound not by chemical forces but mainly by the electric fields of the dipoles.

From the dielectric constant point of view, this behavior may be described as follows: if a polar liquid (say nitrobenzene) is dissolved in a nonpolar liquid (say benzene) the variation of the polarization of the mixture as a function of the concentration of the polar liquid is, in general, not linear. In certain cases the apparent electric moment of the molecules is larger and in other cases smaller than that obtained from an extrapolation at infinite dilution, but is always variable with the concentration. The simplest theory of this effect is that the polar molecules associate to produce a sort of polymerized molecule having a smaller or larger moment depending on the relative orientations of the dipoles forming the complex.[1]

Debye[2] has proposed a simple theory of this effect corresponding to the theory that he and Hueckel have given for electrolytes. However the assumptions he had to make, for instance spherical molecules with the dipole at the center, seem too far from reality to confer much value to the theory according to which the polarization per mole should increase with concentration if association takes place. This however is true experimentally only for alcohols. Another theory apparently less general and with looser foundations has been given by Wolfke.[3]

[1] C. P. Smyth, Chem. Rev. **6**, No. 4, (1929).
[2] Debye, Handbuch der Radiologie, Vol. 6.
[3] Wolfke, Phys. Zeits. **29**, 713 (1928).

It seemed thus commendable to accumulate data on the phenomenon of association before the theory could be advanced very much, hence this investigation.

If an electric field is responsible for the association one would expect it to depend (a) on the temperature, because it controls the motion of the molecules, (b) on the magnitude of the electric moment and (c) on the shape of the molecules. Data available at the present time give information concerning the association of a substance with itself alone.[4] Our experiments investigate the association of one type of molecule with another, in particular with respect to factor (b). Special consideration was given to the association of

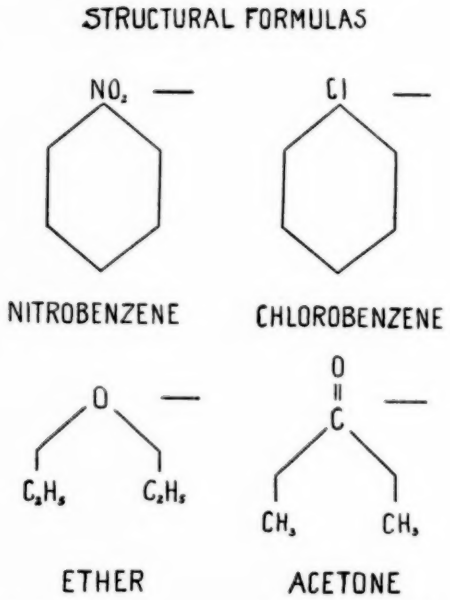

Fig. 1. Structural formulas of the compounds used. Probable polarity indicated.

nitrobenzene[5] ($\mu = 3.90 \times 10^{-18}$) with ether ($\mu = 1.24 \times 10^{-18}$), chlorobenzene ($\mu = 1.52 \times 10^{-18}$) and acetone ($\mu = 2.70 \times 10^{-18}$), μ being the electric moment, in e.s.u. $\times$ cm. The final results of our experiments give some indication of the effect of the electric moment as well as that of the shape of the molecule on the degree of association. The structural formulas, Fig. 1, may be of service when considering the effect of the position of the moment in the molecule.

Simple Theory of the Dielectric Constant of Mixtures

Debye[2] has shown that the dielectric constant, ϵ, of a mixture under all conditions satisfies the equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}(n_1\alpha_1 + n_2\alpha_2 + \cdots) \qquad (1)$$

[4] Rolinski, Phys. Zeits. **29**, 658 (1928).
[5] J. W. Williams, Phys. Zeits. **29**, 178 (1928).

where n_i is the number of molecules of type i per unit volume, and α_i is given by

$$\alpha_i = a_i + \frac{\mu_i^2}{3kT} \tag{1a}$$

where a_i comes from the deformation of the molecules, μ_i is the permanent electric moment, k is Boltzmann's constant and T the absolute temperature.

If we introduce as new variables the mole fraction $f_i = n_i / \Sigma n_i$ and the polarization $P_i = 4\pi N\alpha_i/3$
we get from (1)

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{\Sigma f_i M_i}{d} = \Sigma P_i f_i \tag{2}$$

where M_i is the molecular weight and d the density of the mixture.

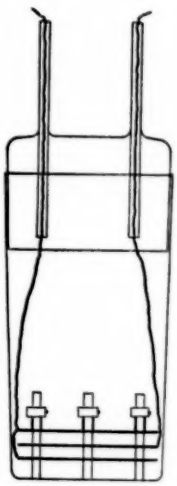

Fig. 2. Sectional view of test condenser and cell.

The theory underlying this formula requires a complete independence of the molecules. If however there is association, we can retain the same expression, assuming then that the apparent moment μ_i varies. Thus the P_i's which are really molecular constants vary also, and their variation may be taken as a measure of the degree of association.

Our experiments consisted in measuring the dielectric constant, ϵ, of mixtures of known concentration f_i. After determining the density, d, the value of P could be obtained.

Apparatus and Procedure

A simple resonance circuit was used in the measurement of the dielectric constant of the mixtures investigated. A standard condenser of 2500$\mu\mu$f and a test condenser (Fig. 2) of approximately 40$\mu\mu$f connected in parallel, constituted the capacity of the absorbing circuit. A quartz crystal oscillator (Fig.

3), wavelength 525 meters, supplied the energy. Resonance was determined by the maximum galvanometer deflection in a galena crystal rectifier circuit tapped across a few turns of the inductance of the absorbing circuit. There

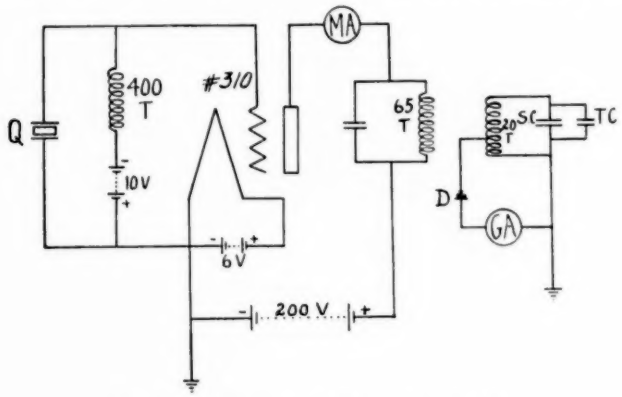

Fig. 3. Oscillator and absorption circuits.

was usually enough energy absorbed from the oscillator to obtain a maximum deflection of 30 to 40 cm, even when only one-tenth of the current passed through the galvanometer.

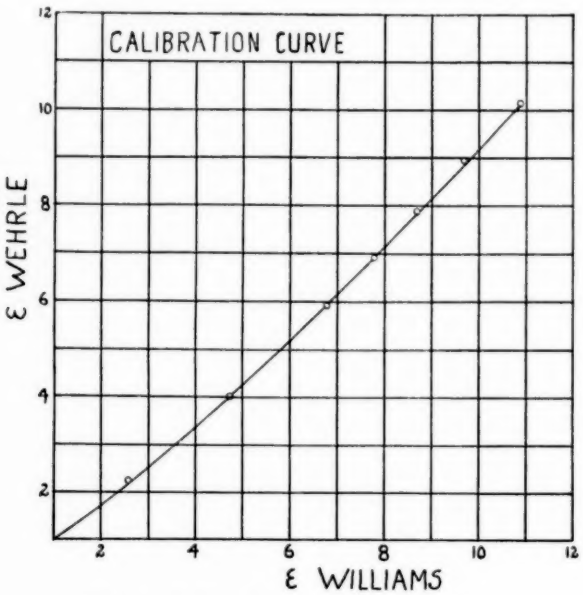

Fig. 4. Calibration curve of test condenser.

The procedure of a test involved the determination of resonance with (a) the standard condenser and the leads of the test condenser in the circuit; (b) the empty test condenser included in the circuit; (c) the mixture under investigation in the test cell.

The uncorrected experimental value of the dielectric constant of any particular solution studied was calculated from the relation

$$\epsilon_s = \frac{C_s}{C_a} = \frac{\frac{\epsilon_s A n}{4\pi d}}{\frac{\epsilon_a A n}{4\pi d}}$$

where C_a, C_s, are capacities of the test condenser with air and with the solution, respectively; ϵ_a, ϵ_s, the corresponding dielectric constants; A, the area per plate of the test condenser; n, the number of plates of dielectric; d, the plate spacing.

Values of dielectric constant for various concentrations of carbon disulphide and nitrobenzene were plotted (Fig. 4) against values, assumed true for the same concentration as reported by J. W. Williams.[6] This plot was taken as the calibration curve of the test condenser and was used in correcting ϵ_s values.

Measurements of ϵ_s were made at a temperature of 25°C $\pm$ 0.5° and could be reproduced in practically all cases to within less than 1 percent. It is to be observed that while the method is quite convenient and of fair accuracy, it proves, in its present form, unsatisfactory for values of dielectric constant above ten. This may be due to any one or possibly both the following causes: (a) once this region of dielectric constant has been attained, the galvanometer deflection has materially decreased and, due to a lack of sensitivity, the motion of the mirror has become relatively sluggish; (b) the introduction of a solution of dielectric constant of the order specified above gives rise to appreciable displacement currents in the dielectric. This is equivalent to adding an effective resistance to the L and C of the pick-up circuit, resulting in a flattening of the resonance peak.

The solutions tested consisted of several series composed of a nonpolar type, benzene, and two polar types, ether and nitrobenzene, chlorobenzene and nitrobenzene or acetone and nitrobenzene. From the stock solutions, test solutions of 150 cc each were prepared containing nitrobenzene in concentration of 0, 2, 4, 6, 8, 10 percent by volume, respectively.

Densities were obtained by means of a Mohr balance. An Abbe refractometer served for the refractive index determination.

Purification of Materials

As it was not the purpose of these experiments to conduct an investigation of the highest precision, but rather to discover some facts about molecular association, the materials used were subjected only to the following purifications.

Benzene. The first sample, thiophene free, was frozen out twice and fractionated. In the case of the second sample, drying with phosphorus

[6] Williams and Ogg, Jour. Amer. Chem. Soc. **50**, 96 (1928).

pentoxide and fractionation yielded a product whose constants were practically identical with those of the sample originally prepared.

Ether. The best grade obtainable was used as supplied by the manufacturer.

Carbon disulphide. After a preliminary agitation with mercury, to remove foreign sulphides, it was dried with phosphorus pentoxide and fractionated.

Chlorobenzene. A sufficient quantity of a high grade material was secured to meet all the needs of the contemplated experiments and was used as supplied.

Acetone. To secure a water-free product, the material was refluxed for three hours over potassium hydroxide and distilled. A further drying over night with fused calcium chloride, refluxing for two hours and fractionation completed the process.

Results

Results are given in Tables I–III. The curves shown are illustrative of the data on benzene, ether and nitrobenzene.

Table I. *Data for solutions of ether and nitrobenzene in benzene.*

f_1	f_2	f_3	ϵ	d	n	P_{123}	P_{23}
1.0000	0.0000	0.0000	2.16	0.8731	1.4980	26.01	0.00
.9825	.0000	.0175	2.62	.8777	1.4995	31.36	5.81
.9648	.0000	.0351	3.04	.8844	1.5001	36.45	11.35
.9472	.0000	.0528	3.40	.8910	1.5012	40.13	15.48
.9294	.0000	.0706	3.80	.8982	1.5026	43.67	19.50
.9115	.0000	.0885	4.18	.9032	1.5037	46.73	23.03
0.8242	0.1758	0.0000	2.55	0.8447	1.472	31.21	9.31
.8094	.1726	.0179	3.00	.8534	1.474	36.65	15.13
.7945	.1694	.0351	3.51	.8608	1.478	41.79	20.67
.7795	.1665	.0540	3.94	.8690	1.481	45.48	24.76
.7647	.1631	.0722	4.35	.8770	1.482	48.53	28.20
.7496	.1599	.0905	4.83	.8843	1.483	51.69	32.56
0.6374	0.3626	0.0000	3.05	0.8141	1.4420	38.21	21.26
.6259	.3560	.0184	3.50	.8220	1.4440	42.87	26.23
.6138	.3492	.0369	3.94	.8301	1.4464	46.71	30.40
.6026	.3428	.0555	4.33	.8383	1.4489	49.75	33.73
.5908	.3361	.0731	4.74	.8473	1.4516	52.41	36.70
.5783	.3290	.0927	5.11	.8557	1.4541	54.68	39.30
0.4386	0.5614	0.0000	3.41	0.7851	1.4174	43.04	31.38
.4303	.5508	.0189	3.98	.7959	1.4197	47.64	36.15
.4220	.5402	.0378	4.30	.8047	1.4223	50.42	39.19
.4137	.5295	.0568	4.78	.8151	1.4268	53.66	42.67
.4054	.5188	.0758	5.22	.8253	1.4303	56.26	45.48
.4011	.5134	.0959	5.63	.8357	1.4333	59.01	48.35
0.2266	0.7734	0.0000	3.88	0.7487	1.3830	49.09	43.21
.2221	.7582	.0196	4.32	.7590	1.3865	52.56	46.78
.2177	.7431	.0392	4.72	.7694	1.3910	55.31	49.65
.2132	.7279	.0588	5.10	.7784	1.3945	57.74	52.20
.2088	.7127	.0784	5.48	.7889	1.3986	59.80	54.37
.2043	.6975	.0981	5.84	.7997	1.4028	61.54	56.22

TABLE I. (*Continued*)

f_1	f_2	f_3	ϵ	d	n	P_{123}	P_{23}
0.0000	1.0000	0.0000	4.55	0.7118	1.3521	56.42	56.42
.0000	.9795	.0205	5.00	.7232	1.3559	59.34	59.34
.0000	.9591	.0409	5.47	.7348	1.3612	61.98	61.98
.0000	.9386	.0613	5.89	.7454	1.3663	64.10	64.10
.0000	.9183	.0817	6.31	.7569	1.3715	65.93	65.93
.0000	.8979	.1021	6.73	.7696	1.3768	67.46	67.46

f_1, f_2, f_3 are mole fractions of benzene, ether and nitrobenzene, respectively; ϵ, n, d are corrected dielectric constant, index of refraction and density, respectively; P_{123} the polarization of the three-component solution calculated from Eq. (2); P_{23} the polarization of ether and nitrobenzene alone, calculated from $P_{23}=P_{123}-f_1 P_1$.

TABLE II. *Data for solutions of chlorobenzene and nitrobenzene in benzene.*

f_1	f_2	f_3	ϵ	d	n	P_{123}	P_{23}
1.0000	0.0000	0.0000	2.16	0.8731	1.4970	26.01	0.00
.9825	.0000	.0175	2.62	.8777	1.4982	31.36	5.81
.9648	.0000	.0351	3.04	.8844	1.4993	36.45	11.35
.9472	.0000	.0528	3.40	.8910	1.5005	40.13	15.48
.9294	.0000	.0706	3.80	.8982	1.5016	43.67	19.50
.9115	.0000	.0885	4.18	.9032	1.5028	46.73	23.03
0.8207	0.1793	0.0000	2.87	0.9156	1.5022	35.34	13.99
.8059	.1761	.0180	3.25	.9208	1.5031	39.54	18.58
.7910	.1728	.0362	3.61	.9274	1.5041	42.88	22.30
.7761	.1696	.0543	3.98	.9334	1.5049	46.11	25.92
.7612	.1663	.0725	4.35	.9388	1.5058	48.92	29.12
.7462	.1630	.0908	4.68	.9452	1.5068	51.16	31.75
0.6318	0.3682	0.0000	3.46	0.9622	1.5072	42.50	26.07
.6202	.3614	.0184	3.83	.9673	1.5080	45.85	29.72
.6080	.3543	.0377	4.13	.9714	1.5088	48.35	32.54
.5968	.3478	.0554	4.50	.9766	1.5097	51.02	35.50
.5850	.3409	.0741	4.82	.9814	1.5105	53.17	37.92
.5731	.3340	.0929	5.18	.9867	1.5113	55.32	40.41
0.4327	0.5673	0.0000	4.06	1.0079	1.5108	48.91	37.65
.4245	.5566	.0189	4.39	1.0113	1.5115	51.46	40.42
.4163	.5458	.0379	4.73	1.0150	1.5123	53.83	43.00
.4081	.5350	.0569	5.04	1.0193	1.5129	55.77	45.16
.3998	.5242	.0760	5.33	1.0230	1.5133	57.48	47.08
.3915	.5133	.0952	5.68	1.0269	1.5141	59.37	49.19
0.2224	0.7776	0.0000	4.58	1.0510	1.5173	54.28	48.49
.2181	.7625	.0194	4.84	1.0547	1.5179	56.01	50.34
.2142	.7472	.0386	5.21	1.0578	1.5184	58.25	52.69
.2094	.7321	.0585	5.51	1.0603	1.5190	59.99	54.54
.2051	.7169	.0780	5.83	1.0635	1.5196	61.64	56.31
.2007	.7017	.0976	6.11	1.0667	1.5201	62.99	57.77
0.0000	1.0000	0.0000	5.22	1.0997	1.5227	58.90	58.90
.0000	.9685	.0315	5.51	1.1017	1.5231	61.48	61.48
.0000	.9488	.0512	5.84	1.1034	1.5236	63.28	63.28
.0000	.9290	.0710	6.13	1.1052	1.5240	64.65	64.65
.0000	.9092	.0908	6.40	1.1073	1.5245	65.85	65.85
.0000	.8895	.1105	6.72	1.1087	1.5250	67.27	67.27

f_1, f_2, f_3 are mole fractions of benzene, chlorobenzene and nitrobenzene, respectively; ϵ, n, d are corrected dielectric constant, index of refraction and density, respectively; P_{123} the polarization of the three-component solution calculated from Eq. (2); P_{23} the polarization of chlorobenzene and nitrobenzene alone, calculated from $P_{23}=P_{123}-f_1P_1$.

TABLE III. *Data for solutions of acetone and nitrobenzene in benzene.*

f_1	f_2	f_3	ϵ	d	n	P_{123}	P_{23}
1.0000	0.0000	0.0000	2.16	0.8731	1.4980	26.01	0.00
.9825	.0000	.0175	2.62	.8777	1.4995	31.36	5.81
.9648	.0000	.0351	3.04	.8844	1.5001	36.45	11.35
.9472	.0000	.0528	3.40	.8910	1.5012	40.13	15.48
.9294	.0000	.0706	3.80	.8982	1.5026	43.67	19.50
.9115	.0000	.0885	4.18	.9032	1.5037	46.73	23.03
0.8806	0.1194	0.0000	3.48	0.8632	1.4827	39.68	16.77
.8655	.1173	.0172	3.82	.8695	1.4838	42.64	20.13
.8503	.1153	.0344	4.31	.8770	1.4848	46.24	24.12
.8350	.1132	.0518	4.52	.8837	1.4862	47.74	26.02
.8196	.1111	.0693	4.90	.8906	1.4871	50.12	28.80
.8041	.1090	.0869	5.23	.8979	1.4885	51.96	31.05
0.7663	0.2337	0.0000	4.70	0.8541	1.4668	47.46	27.53
.7534	.2298	.0168	5.03	.8616	1.4686	49.39	29.80
.7404	.2258	.0338	5.31	.8687	1.4704	50.96	31.70
.7273	.2218	.0509	5.65	.8757	1.4720	52.71	33.79
.7141	.2178	.0681	5.96	.8824	1.4738	54.22	35.65
.7009	.2138	.0853	6.26	.8892	1.4753	55.60	37.37
0.6567	0.3433	0.0000	5.93	0.8458	1.4534	52.33	35.25
.6459	.3376	.0165	6.26	.8535	1.4553	53.77	36.97
.6349	.3319	.0332	6.55	.8611	1.4577	54.98	38.46
.6239	.3262	.0499	6.83	.8679	1.4594	56.14	39.91
.6130	.3205	.0665	7.12	.8751	1.4613	57.25	41.31
.6017	.3146	.0837	7.47	.8822	1.4634	58.51	42.86

f_1, f_2, f_3 are mole fractions of benzene, acetone and nitrobenzene, respectively; ϵ, n, d are corrected dielectric constant, index of refraction and density, respectively; P_{123} the polarization of the three-component solution calculated from Eq. (2); P_{23} the polarization of acetone and nitrobenzene alone, calculated from $P_{23}=P_{123}-f_1 P_1$.

Values of P_{23} were plotted against mole fraction of nitrobenzene at constant ether, and against mole fraction of ether at constant nitrobenzene. They were obtained from P_{123} by subtracting the polarization due to benzene, which is known to remain constant, as it is nonpolar and does not associate. P_{23} then represents the polarization due to the polar substances and can be expressed as

$$P_{23} = f_2 P_2(f_2, f_3) + f_3 P_3(f_2, f_3). \tag{3}$$

P_2 and P_3 are written explicitly as functions of f_2 and f_3 because they associate and because the association depends upon the concentration. Differentiating (3) with respect to f_2 and putting $f_2 \rightarrow 0$, we obtain

$$\left(\frac{\partial P_{23}}{\partial f_2}\right)_{f_2 \rightarrow 0} = (P_2(f_2, f_3))_{f_2 \rightarrow 0} + \left(\frac{\partial P_3(f_2, f_3)}{\partial f_2}\right)_{f_2 \rightarrow 0}$$

and a similar expression for

$$\left(\frac{\partial P_{23}}{\partial f_3}\right)_{f_3 \rightarrow 0}.$$

Illustrative curves are presented in Figs. 5, 6, 7, 8. The fact that the curves vary with f_3 or f_2 shows definitely that P_2 and P_3 are both functions of f_3 and f_2,

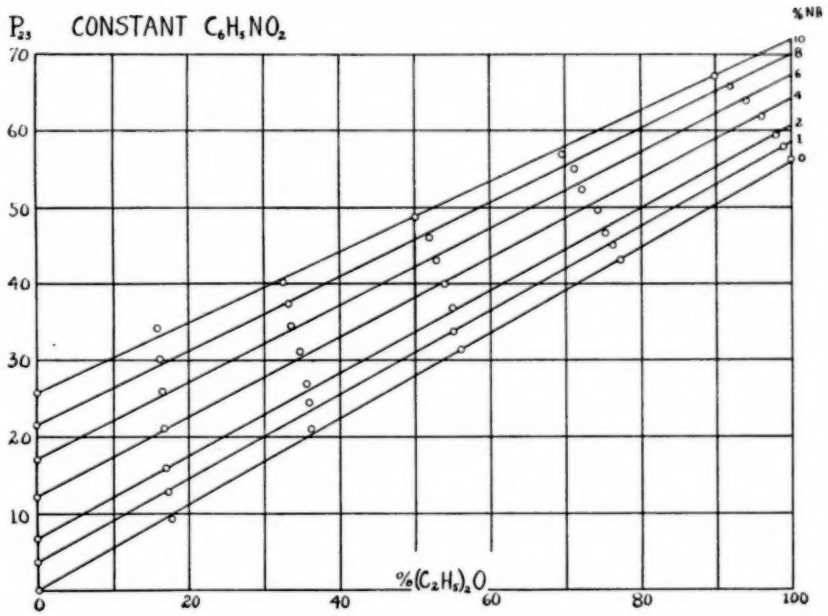

Fig. 5. Polarization, P_{23}, of nitrobenzene and ether in benzene against percent ether for several constant percentages of nitrobenzene.

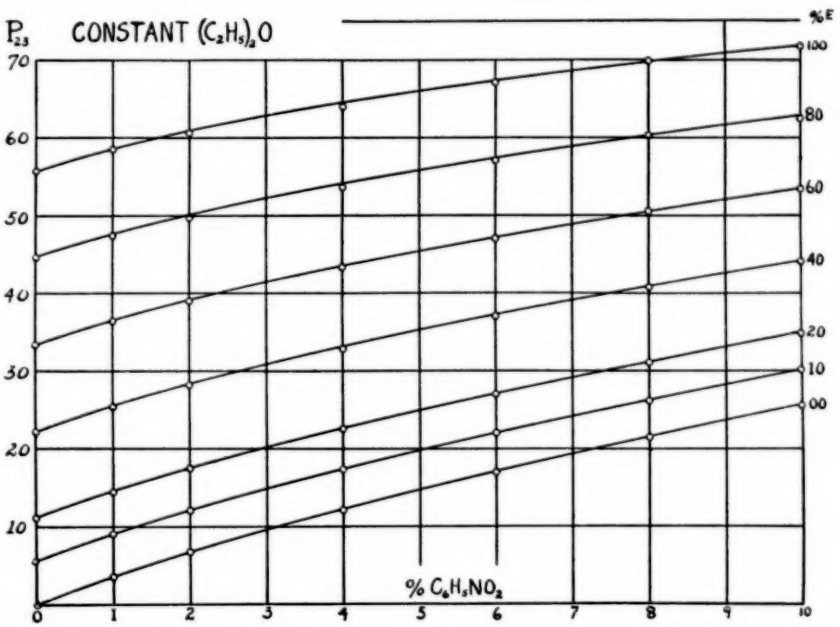

Fig. 6. The data of Fig. 5 differently presented showing polarization, P_{23}, of nitrobenzene and ether in benzene against percent nitrobenzene for several constant percentages of ether. The curve for 100 percent ether is plotted from extrapolated physically impossible, portions of Fig. 5.

which means that nitrobenzene does associate with ether. If there were no association,

$$\left(\frac{\partial P_{23}}{\partial f_2}\right)_{f_2 \to 0} \quad \text{and} \quad \left(\frac{\partial P_{23}}{\partial f_3}\right)_{f_3 \to 0}$$

should be constant as P_2 would then not be function of f_3 nor P_3 function of f_2.

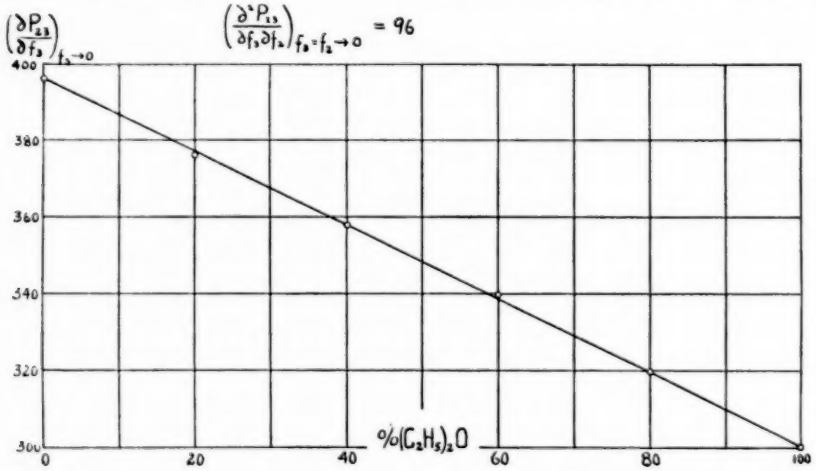

Fig. 7. Plot of the slopes of the curves of Fig. 6 at f_3, the concentration of nitrobenzene approaching zero. The slope of Fig. 7 is an approximate relative measure of the association of ether and nitrobenzene.

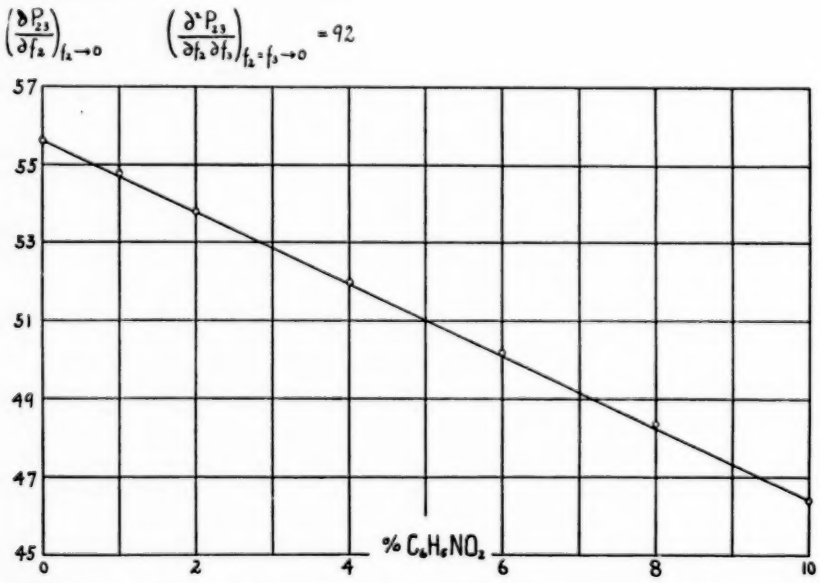

Fig. 8. Plot of the slopes of the curves of Fig. 5 at f_2, the concentration of ether approaching zero. The slope of Fig. 8 is an approximate relative measure of the association of nitrobenzene and ether. Note the corresponding value in Fig. 7.

Thus the curves are a definite proof of the association of nitrobenzene with ether, chlorobenzene and acetone. We can take the slopes of these curves, at

zero concentration, as an approximate relative measure of the degree of association. For this slope we write

$$a = \left(\frac{\partial^2 P_{23}}{\partial f_2 \partial f_3} = \frac{\partial P_2}{\partial f_3} + \frac{\partial P_3}{\partial f_2}\right)_{f_2 = f_3 = 0}. \tag{4}$$

This quantity furnishes us a numerical estimate of the extent to which the polarizations depend on the concentration. From our data these results follow:

TABLE IV.
Association of nitrobenzene with

Substance	$\mu 10^{18}$	a
Nitrobenzene	3.90	1185
Acetone	2.70	690
Chlorobenzene	1.52	270
Ethyl ether	1.24	94

As was expected, the larger the moment, the more pronounced was the association. It seems that the most important factor determining the degree of association is the electric moment of the molecule.

Another question presents itself at this point. Do the association molecules share their electrons or not? The relation $\epsilon = n^2$ allows an answer. The calculation of P_∞ from Eq. (2), replacing ϵ by n^2 and omitting the term $\mu_i^2/3kT$ of (1a) gives

$$P_\infty = \frac{n_1^2 - 1}{n_1^2 + 2}\frac{M_1 f_1}{d_1} + \frac{n_2^2 - 1}{n_2^2 + 2}\frac{M_2 f_2}{d_2} + \frac{n_3^2 - 1}{n_3^2 + 2}\frac{M_3 f_3}{d_3} \tag{5}$$

calculated on the basis that the components act individually and

$$P_\infty' = \frac{n_4^2 - 1}{n_4^2 + 2}\frac{M_1 f_1 + M_2 f_2 + M_3 f_3}{d_4} \tag{6}$$

on the basis that the components act collectively, where n_1, n_2, n_3, n_4, and d_1, d_2, d_3, d_4 are the refractive indices and densities of benzene, ether, nitrobenzene, and the mixture of the three under consideration, P_∞ is the polarization at infinite dilution. The comparison results in values which check within the limits of experimental errors. An illustrative example of the comparison of P_∞, from Eq. (5), and P_∞', from Eq. (6), for a mixture of benzene, ether and nitrobenzene is given in Table V.

TABLE V.

f_1	f_2	f_3	n_4	d_4	P_∞	P_∞'
0.6374	0.3626	0.0000	1.4418	0.8141	24.87	24.89
.6259	.3560	.0184	1.4440	.8220	25.02	25.05
.6138	.3492	.0369	1.4464	.8301	25.16	25.18
.6026	.3428	.0555	1.4489	.8384	25.33	25.35
.5908	.3361	.0731	1.4516	.8473	25.44	25.46
.5783	.3290	.0927	1.4541	.8557	25.59	25.61

Hence it is to be concluded that there is no sharing of electrons in this process.

Conclusion

Before anything more definite can be obtained from the measurements, a working hypothesis as to the true nature of association must be formulated. Such a project is at present under investigation.

Acknowledgment

The author wishes to thank Dr. Weigle, who suggested this problem, and the members of the Physics department for their kind cooperation.

NOTES ON THE EFFECT OF DISTANCE FROM THE SOURCE ON THE VELOCITY OF SOUND AT ULTRASONIC FREQUENCIES

By Charles D. Reid
Cruft Laboratory, Harvard University

(Received March 20, 1931)

Abstract

Measurements of the velocity of ultrasonic waves have been made at a greater distance than heretofore. It is found to be independent of frequency within 0.01 percent which is the error of measurement.

In a previous paper[1] a method of obtaining the velocity of ultrasonic waves was described. It was found that when measurements were taken in proximity to the face of the sound-emitting crystal the resulting velocity was higher than that calculated from data obtained in a region more remote from the face. It was also noted that this effect was more marked as the frequency decreased. Hence it seemed desirable to continue the measurements in a region still more remote from the sound source, since the previous work indicated that an asymptotic value had almost been reached.

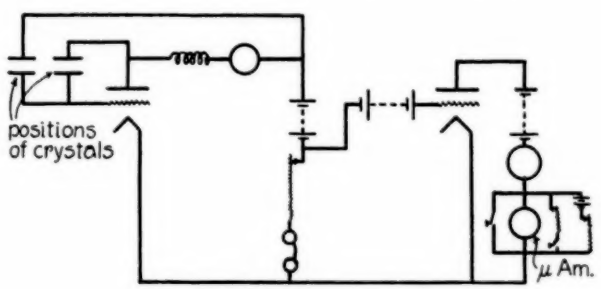

Fig. 1. Direct current amplifier.

With this in mind, the length of the sound chamber was doubled, and a direct current amplifier (shown in Fig. 1) was constructed in order to detect the sound energy at this increased distance. By using the proper grid bias on the amplifier tube the change in plate current produced by the motion of the reflector was increased by a factor of ten.

With the use of this amplifier, the measurements recorded here were made from the data secured in the region between 50 centimeters and 100 centimeters from the sound source.

To obtain satisfactory stationary wave-trains in this region it was found necessary to pad the inside of the sound chamber with acoustic felt to reduce

[1] C. D. Reid, Phys. Rev. **35**, 814 (1930).

the effect of reflected energy from the walls. This prevented the use of dry air in the present experiments as it has been found difficult to dry out the felt. However, the felt lining does maintain the humidity at a constant value and the experimental results have been corrected for this humidity.

In order to determine the value of the humidity thus obtained, a hair hygrometer was calibrated over a small range of humidities by placing it under a bell jar with two different saturated salt solutions and assuming that the motion of the hygrometer needle in the interval between these fixed humidities to be a linear function of the humidity.

The results of these measurements are recorded in Table I.

TABLE I. *The velocity of sound in moist air free from carbon dioxide.*

Frequency	No. of runs	Velocity at 0°C
140	2	332.09
105	7	332.05
84	3	332.12
70	4	332.05
60	2	332.01
42	4	332.15

Average velocity at 0°C 332.08 ± 0.02 meters/sec.
Relative humidity 32 per cent
Velocity in dry air at 0°C—$V_H - 0.014\ H = V_0$
$332.08 - 32 \times 0.014 = 331.63$ meter/sec.

From the figures recorded in Table I it may be concluded that the velocity of sound in the frequency range included is constant within 0.01 percent when the measurements are carried out in a region sufficiently remote from the source.

When the velocity obtained in this manner is corrected for humidity by use of the relation determined by previous experiments it is found to agree with the former results within experimental error. This serves as a check on the humidity formula.

The above experiments have been carried on under the direction of Dr. G. W. Pierce.

THE POLARIZATION AND THE ELECTRIC MOMENT OF TUNG OIL[1]

By A. A. Bless
University of Florida

(Received March 12, 1931)

Abstract

The molar polarization of tung oil was determined by the method of mixtures using the relation $P_{1,2}=[(\epsilon-1)/(\epsilon+2)]\,(M_1f_1+M_2f_2)/d=P_1f_1+P_2f_2$ where ϵ is the dielectric constant; d the density of the solution; f_1f_2, M_1M_2, and P_1P_2 are respectively the mole fraction, the molecular weight and the polarization of the two components. The molar polarization of tung oil is 360 cc and the moment is 2.29×10^{-18} e.s.u. Eq. (1) is derived with the simplifying assumption that the internal field of the molecules may be neglected. It applies only to gases and to very dilute solutions, where the molecules are far apart. It is found that in the case of tung oil Eq. (1) applies for all concentrations, showing that the clustering of the molecules is such as to neutralize the internal field. The values of the moment of tung oil and of ethyl ether were determined from the variation of the polarization with temperature using the relation $P=(4\pi N/3)(\alpha+\mu^2/3KT)$ where P is the molar polarization, α the molecular polarization, N Avogadro's number, K Boltzmann's constant, T the absolute temperature and μ the electric moment. The values do not agree at all with those obtained by the method of mixtures. Similar disagreement was observed by other experimenters. The explanation is suggested that the internal field is never completely eliminated, and that the residual field being a function of the temperature makes Eq. (2) inapplicable even to dilute solutions.

Method of Mixtures

THE molar polarization of a mixture of two substances is given by[2]

$$P_{1,2}=\frac{\epsilon-1}{\epsilon+2}\,\frac{M_1f_1+M_2f_2}{d}=P_1f_1+P_2f_2 \qquad (1)$$

where f_1, f_2 and M_1, M_2 and P_1P_2 are, respectively, the mole fraction, the molecular weight and the polarization of the two components; d is the density and ϵ the dielectric constant of the solution. Since $f_1=1-f_2$, Eq. (1) may also be written in the form

$$P_{1,2}=f_2(P_2-P_1)+P_1. \qquad (2)$$

showing that $P_{1,2}$ is a linear function of f_2. Eq. (1) is deduced from the Clausius-Mosotti relation, that the quotient $(\epsilon-1)/(\epsilon+2)$ is proportional to the density. This relation is derived with the simplifying assumption that the internal electric field of the molecules may be neglected. In case of polar substances, equation (1) would be applicable only when the molecules are far

[1] Paper read at the meetings of the Committee on Electrical Insulation of the National Research Council, November 7, 1930.

[2] P. Debye, Polar Molecules, the Chemical Catalog Co., 1929.

apart, as in gases or in dilute solutions of a polar substance in a nonpolar solvent. $P_{1,2}$ is proportional to f_2 only when f_2 is a small fraction. The departure from proportionality between $P_{1,2}$ and f_2 for high concentrations of the polar substance may be taken as indicating the interaction of molecular fields. To find the polarization of a liquid substance the procedure is to dissolve the polar substance in a nonpolar solvent, determine the polarization for increasing mole fractions of the solute and then extrapolate for infinite dilution. This method was used to determine the electric moment of tung oil using benzene as the nonpolar solvent.

The quantities which are measured experimentally are the density and the dielectric constant of the solutions. The density was determined by the pyknometer method with an accuracy of about 0.02 percent. The dielectric constant was found in the usual manner, from the measured capacity of the test cell in air and in the liquid, the capacities being determined by the substitution method.

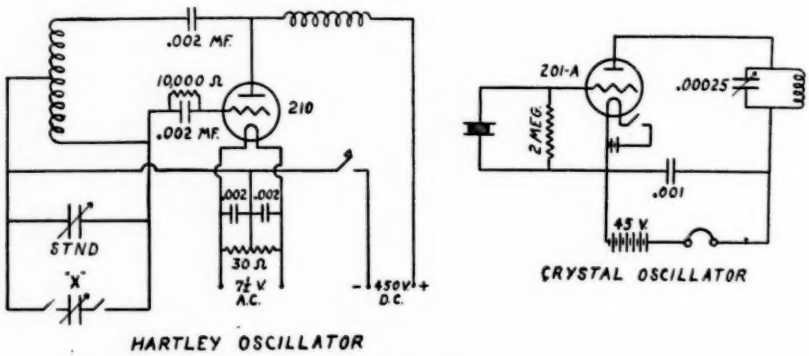

Fig. 1. The circuit for measuring the capacity of the cell.

Two different circuits were used for finding the dielectric constant of the solutions. In the first circuit a Hartley oscillator was used as a source of oscillations, the frequency being measured with a standard General Radio wave meter. In the receiving circuit a small aluminum condenser of known capacity placed in a vessel containing the solution was connected in parallel with a standard General Radio precision condenser. The receiving circuit was first tuned to resonance with the oscillator with both condensers in parallel and then retuned again to resonance with the standard alone in the circuit. The difference between the two readings of the condenser gave the capacity of the aluminum cell. These measurements were made for three different frequencies, 10^5, 3×10^5, 10^6. The accuracy of this method was about 1 percent.

The accuracy was very greatly increased when a heterodyne beat method was substituted for the above. The oscillations were kept at a constant frequency by the aid of a quartz crystal oscillator. A Hartley oscillator containing the test cell and the precision condenser was tuned to beat with the crystal set, the disappearance of the note indicating resonance. The capacity of the test cell was found in the same manner as in the first circuit. The polarization

of the solution was then calculated from the data using relation (1). The circuit is shown in Fig. 1.

The tung oil used in these experiments was obtained from the Chemistry Department of this University. Several samples of the product were tried, all giving very consistent results.

Data obtained using the Hartley oscillator are given in Table I.

TABLE I.

		$\nu=10^5$		$\nu=5\times10^5$		$\nu=10^6$	
f	d	ϵ	P	ϵ	P	ϵ	P
0.0000	0.878780	2.258	25.98	2.260	26.20	2.258	25.98
.0082	.8806	2.278	29.01	2.270	28.18	2.280	29.50
.0318	.8922	2.470	39.04	2.452	38.60	2.452	38.60
.0840	.9076	2.602	52.82	2.675	54.30	2.701	55.83
.2300	.9227	2.901	100.20	2.920	101.20	2.930	102.00
.4270	.9297	2.960	162.00	3.012	165.50	3.045	167.50
.7900	.9337	3.065	279.80	3.140	286.00	3.142	286.60
1.0000	.9363	3.170	356.80	3.178	358.00	3.172	357.00

Data obtained by the heterodyne beat method are shown in Table II.

TABLE II.

	$\nu=1.47\times10^6$		
f	d	ϵ	P
0.0000	0.8751	2.265	26.44
.0165	.8888	2.341	31.25
.0556	.9001	2.624	45.70
.1655	.9172	2.892	73.70
.3835	.9275	3.192	144.5
.6643	.9344	3.214	233.5
1.0000	.9356	3.230	361.5

In Figs. 2 and 3 the polarization of the solutions is plotted against the mole fraction of the tung oil. The value of the polarization is about 360 cc.

The polarization of a substance is the result of the distortion of the molecules due to electronic displacements produced by the field, and of the orientation of the polar molecules in the impressed field. At very high frequencies the molecules are no longer able to follow the field and the contribution to the polarization due to the oriented molecules vanishes. At optical frequencies only the electrons are affected and the dielectric constant may therefore be identified with the square of the refractive index. The contribution to the polarization due to the orientation of the polar molecules may be found by subtracting from the total polarization the part which is due to the distortion effect of the field, and which is given by:

$$P_0=\frac{r^2-1}{r^2+2}\cdot\frac{M}{d}$$

where r is the refractive index of the solution, and the electric moment of the molecules may be found from the relation

$$\mu = 0.0127 \times 10^{-18}[(P - P_0)T]^{1/2}$$

giving a value for $\mu = 2.29 \times 10^{-18}$ e.s.u.

It must be observed that as tung oil in itself is a mixture of at least two substances, the value of the electric moment found above must be considered as a weighted mean of the component molecules.

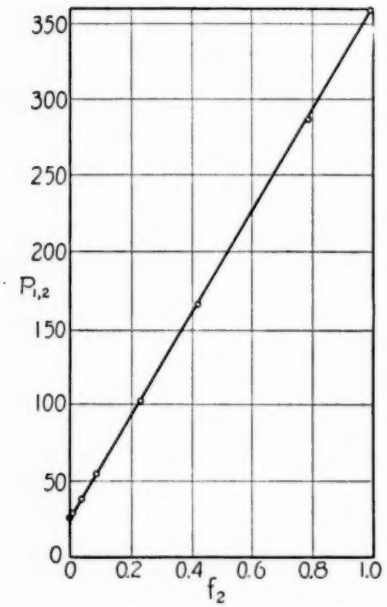

Fig. 2. Polarization vs. mole fraction of tung oil for $\gamma = 5 \times 10^5$ cycles/sec.

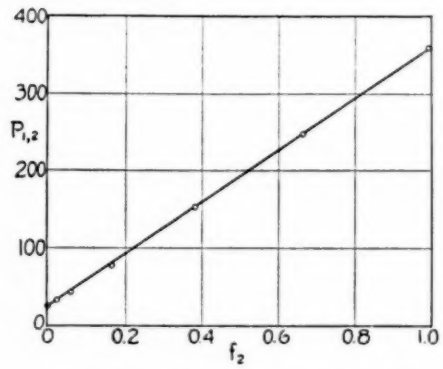

Fig. 3. Polarization vs. mole fraction $\gamma = 1.47 \times 10^6$ cycles/sec.

Variation of Polarization with Temperature

The graph of the polarization versus mole fraction is a straight line showing that the Clausius-Mosotti relation may be applied for all concentrations of tung oil in benzene. The tung oil molecules are evidently present in the solution in clusters so formed as to neutralize the internal field. This clustering is probably similar to the one observed by Stewart[3] and his collaborators. It seemed interesting to investigate the effect of temperature on the clustering of these molecules. Some of these experiments will now be described.

It is possible to find the electric moment in another manner. From the Debye theory it follows that the polarization of a substance is given by:

$$P = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT}\right) \tag{3}$$

where N is Avogadro's constant, α the molecular polarization, K Boltzmann's constant, T the absolute temperature. If a substance is polar its polarization will be directly proportional to the reciprocal of the absolute temperature.

[3] G. W. Stewart and R. M. Morrow, Phys. Rev. **30,** 232 (1929).

If the polarization is measured in the manner described above for a range of temperatures the molecular moment may be calculated from the slope of the straight line obtained when P is plotted against $1/T$, since $P=a+(b/T)$, where b is the slope of the line $=4\pi N/9)(\mu^2/K)$.

The condenser used in these experiments is shown in Fig. 4. It consisted of two concentric nickel cylinders placed in two concentric glass tubes, A and B, sealed at the bottom. The glass tubes were of such a diameter that the outer nickel cylinder was just large enough to fit inside the outer glass tube while the smaller nickel cylinder fitted tightly around the inner tube. This arrangement gave a condenser of fairly large capacity for a very small volume of fluid between the nickel cylinders. A third glass tube C for housing the thermometer was sealed to B. A small tube D was sealed to the junction of B and C. It provided a vent for the escape of the air entrapped between B

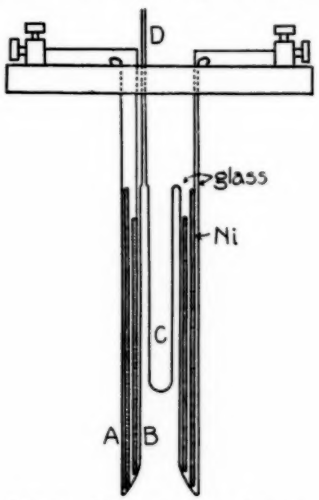

Fig. 4. Diagram of condenser.

and C when the condenser was lowered into the cooling solution, thus enabling the solution to reach every part of the condenser.

A solution of alcohol and solid carbon dioxide was used as the cooling solution. The air capacity of the cell was 69.3 cm. The cooling solution was kept in a large Dewar flask. Measurements of the capacity of the cell were taken only when the temperature shown by the thermometer placed in C differed by a fraction of a degree from the reading of the thermometer placed directly in the solution.

Eq. (3) just like Eq. (1) applies only when the internal field of the molecules may be neglected. And to use this relation dilute solutions must be employed. However, as tung oil showed no molecular interaction the substance was used in the undiluted state.

Fig. 5 is the graph of the data. The plot is sensibly a straight line. The moment calculated from the slope of the straight line was about twice as large as the value found from the method of mixtures. No shifting of the straight line could account even for a fraction of the discrepancy.

Ethyl ether is another substance the molecules of which show no interaction at ordinary temperatures. Its moment as determined by Krchma and Williams[4] using the method of mixtures is 1.24×10^{-18} e.s.u. Experiments were made to measure the moment of ethyl ether using the method of the variation of the polarization with temperature. The value of the moment comes out about 60 percent higher.

These experiments show that the peculiar arrangement of the molecules which neutralizes the internal field at a given temperature is modified when the temperature is changed. The molecular field is not completely eliminated.

Even dilute solutions of a substance, where the molecules are relatively far apart, show some interaction, which varies with temperature. The discrepancy between the value of the moments of some molecules, using the method of mixtures and the method of variation of the polarization of dilute

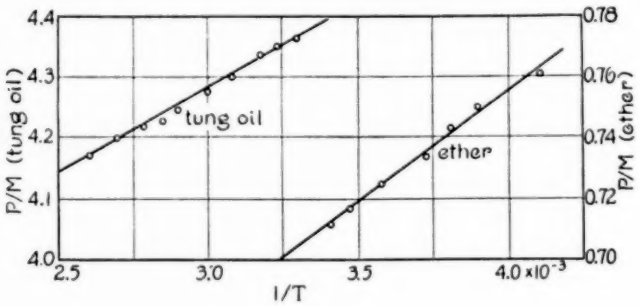

Fig. 5.

solutions with temperature in the experiments of Smyth and Morgan[5], is probably due to this cause, and not, as these authors suggest, to the inaccuracy of measurements. A similar discrepancy was observed by Morgan[6] in his measurements of the moments of some methyl halides by the two methods. The difference in the values obtained is much larger than the experimental error. One is forced to the conclusion, therefore, that even in dilute solutions, which at a given temperature seem to show no interaction, the internal field is not completely absent, and the field manifests itself in the variation of the moment with temperature. It is of interest to find the degree of dilution needed to show no temperature effect of the polarization. Experiments along this line are now being carried out in this laboratory.

Some of the apparatus used in these experiments were purchased by the aid of the Sigma Xi grant. The author wishes to express his gratitude to the Committee on Awards for the grant.

[4] I. J. Krchma and J. W. Williams, Jour. Amer. Chem. Soc. **49**, 2408 (1927).

[5] C. P. Smyth and S. O. Morgan, Jour. Amer. Chem. Soc. **50**, 1547 (1928).

[6] S. O. Morgan, paper read at the meetings of the Committee on Insulation of the National Research Council, November 7, 1930.

AN EXPERIMENTAL STUDY OF KUNDT'S TUBE DUST FIGURES

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(Received February 24, 1931)

Abstract

An experimental study of the dust striations in a Kundt's tube has been carried out using a loud speaker, operated from a vacuum tube oscillator, as a source of sound. It is found that the positions of the vibrator for maximum agitation of the dust is different for the case in which a loud speaker is used from that obtained when a stroked rod is used. The formation and behavior of the striations is described in detail. It is found that the spacing between the striations increases with the intensity of sound, decreases with an increase in pressure of the gas, and decreases with an increase in density of the dust material. A minimum spacing is found when the size of the dust particles is changed. The relation suggested by Cook that the ratio of the separation of the striations to the mean free path is a constant was tested but the results obtained indicated that such a simple relation does not exist.

I. Introduction

In 1866 Kundt[1] showed that when standing sound waves were excited in a closed resonance tube, dust particles in the tube arranged themselves in the form of striations perpendicular to the axis of the tube. Since that time however, very little information has been obtained on these striations due to the fact that accurate measurements could only be made after the vibrations had ceased. With the general introduction of the loud speaker as a source of sound[2] and the use of a vacuum tubes oscillator as a means of excitation, it has become possible to examine the phenomena in the Kundt's tube in a far more accurate manner.

The cause of the striations in the Kundt's tube has never been completely determined. The hydrodynamical theory of the oscillations of the air column has been studied by König and others, but after reading these papers, one still wonders how the striations are really produced. However before a rigorous quantitative theory can be developed it is necessary to have accurate measurements of the positions of the striations under different experimental conditions. It is the purpose of this paper to help bridge this gap in our experimental knowledge of the behavior of dust striations.

Before the experimental procedure is taken up it must be emphasized that there is a distinct difference in the behavior of the striations when produced by a stroked rod and when produced by a loud speaker operated from a vacuum tube oscillator. If a stroked rod is used, the maximum agitation of the dust occurs when the vibrating end of the rod is placed at a node, and the

[1] A. Kundt, Pogg. Ann. **127,** 497 (1866).
[2] A. B. Wood, A Textbook of Sound, New York, 1930.

agitation is minimum when the vibrator is at an antinode. However, when the loud speaker is used maximum agitation is obtained when the vibrator is one-third of a segment from a node and a minimum when the vibrator is at a node. Furthermore, after continued stroking of a rod the dust particles in the tube gather into small heaps at the nodes[3] while with the loud speaker there is no indication of this phenomena at all even after long periods of operation. In the work of E. J. Irons[4] in which a stroked rod was used, the formation of rings or disks extending across the diameter of the tube at the nodes is very beautifully shown.

With a loud speaker unit, it was found possible to produce such rings[5] but they were always at the antinodes instead of at the nodes. By using extremely light dust and greater intensity of sound, these rings could be made to assume the appearance of disks with much greater density at the periphery than at the center of the tube. Each ring always lies in the plane of the central stria and seems to be a continuation of it. These rings mark the midpoint of the

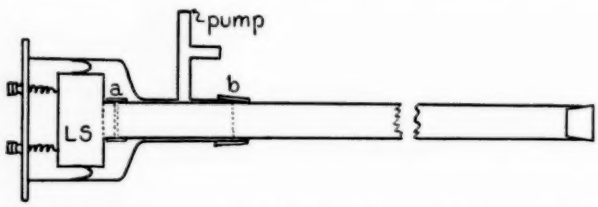

Fig. 1. Experimental arrangement to obtain dust figures in a resonating tube under various pressures. *LS* indicates the loud speaker held in place by springs, *a* and *b* represent short pieces of heavy rubber tubing used to hold the tubes in place.

antinodal region very sharply and are therefore of great value in determining the length of a segment. The motion of the dust particles constituting a ring is from the extremities of the central stria around the wall of the tube toward the top. Neighboring striae usually have dust particles streaming off from their extremities also and these are continually fed into the antinodal ring. Sometimes neighboring striae can be made to produce these rings but they are never so perfect as the central one. After a central ring has been established, it is possible by shifting the stop slowly to drive all the dust from the antinodal region, except that constituting the ring and its disk. In this way, an antinodal ring without the accompanying striae may be obtained.

II. Apparatus and Procedure

The apparatus used in this investigation is shown diagrammatically in Fig. 1. A Temple radio loud speaker unit, actuated by a Hartley vacuum tube oscillator, was used as the source of sound. To permit variation of the pres-

[3] Cf. E. J. Irons, Phil. Mag. **7,** 523 (1929).

[4] Reference 3, plate IX, Figs. 2c and 2d.

[5] These disks were first discovered by the writers in 1928. Since then E. Andrade and S. H. Lewar have published independently an account of these disks in Nature, **124,** 724 (1929). See also the recent note of R. V. Cook, Phys. Rev. **36,** 1099 (1930).

sure and to facilitate the changing of the gas in the tube, the loud speaker unit was mounted in a glass cylinder as shown. The frequency of the sound emitted could be varied throughout a sufficiently wide range to secure almost any wave-length desired. Observations were made both under conditions of resonance and of nonresonance.

Pith, cork, Kieselsaure and white sand were found to be the most satisfactory materials for dust. Mustard seed and timothy seed served very well for small spheroids and ellipsoids, respectively. Uniformity of size of dust particles was obtained by sifting the dust through a nest of sieves ranging from 10 to 120 meshes to the inch. A metric scale was placed alongside the tube and when photographed simultaneously with the dust, made measurements of length convenient. The tubes used were 22 mm and 30 mm in diameter, respectively. Their lengths varied from 2.5 to 4 ft. Two 400-watt in-

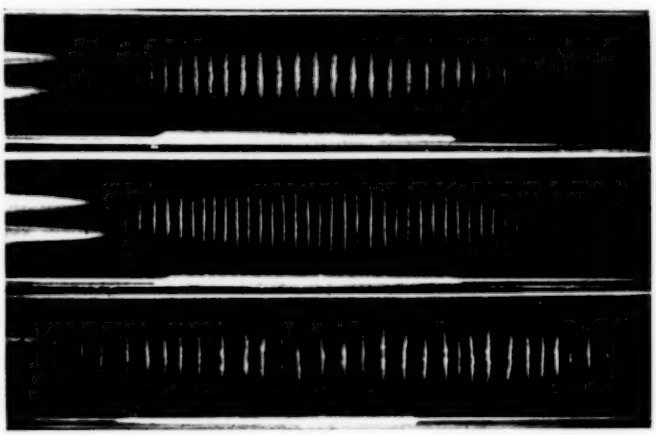

Fig. 2. The appearance of the striations formed when a Kundt's tube is operated by means of a loud speaker. These striations were obtained under atmospheric pressure with a frequency of approximately 1500 sec. The diameter of the dust particles in the middle photograph is intermediate between those in the outer photographs showing that the spacing between the striations does not increase monatonically with the size of the particles.

candescent lamps, equipped with reflectors, were used to illuminate the tube from above for the taking of the photographs. A $4'' \times 5''$ plate camera was used and exposures were usually from 1/50 to 1/100 of a second. A dividing engine was used for measuring the distance between striae.

III. General Appearance and Properties of the Striae

The general appearance of the striae produced by means of a loud speaker element is shown in Fig. 2. With the aid of a lens the striae are often found to be just one layer of particles in thickness. According to the observations of Cook,[6] these particles have a repulsion for each other and are always slightly separated from each other during the continuance of the sound. The present

[6] S. R. Cook, Phil. Mag. **3,** 47 (1902).

investigation failed to substantiate Cook's observations. In every case, whether the particles used were dust, pith spheroids, pith cylinders, sealing-wax spheroids, mustard seed spheroids, or timothy seed ellipsoids, the particles remained in contact during the continuance of the sound, just as if there were a force of attraction between them. This is in conformity with König's[2] theory which assumes a force of attraction between particles whose line of centers is at right angles to the direction of the sound propagation. Ellipsoidal particles always aligned themselves so that their major axes are at right angles to the direction of sound propagation.

Similarly, if thin pith disks about the size of a dime are used in the place of dust, they come to a verticle position in the tube and are rotated till their planes make a right angle with the direction of propagation of the sound. They space themselves much like the dust striae, except that they are farther apart. Usually three or four of these disks are drawn into the middle of the antinode to form the central stria edge to edge and rotate about the axis of the tube like a Dutch windmill. Often other disks, spaced along the tube will also rotate; some turning clockwise, others counter-clockwise.

The dust particles, constituting a stria seem to be in continual oscillation so that some are always freeing themselves from one stria and joining a neighboring one. This interchange of particles is more or less mutual, so that a stria receives just about as many particles as it loses and therefore maintains a rather constant size. Striae tend to diminish both in length and height in going from the antinode to the node.

The position of a stria in a segment may be either constant or variable, depending on the adjustment of the vibrator relative to a node and the stria may form either a straight line across the tube or a curved one, depending on the above adjustment and also on its position in the segment. The central stria always extends straight across the tube, forming a right angle with its axis. This is usually true also of a relatively large number of striae on either side of the central one. The striae near the extremities however, tend to be more or less curved; sometimes being concave toward the nodes and sometimes concave toward the antinodes, depending on the position of the vibrator relative to a node.

When cork dust (size 80–100 mesh) is piled at the nodes and the vibrator of the loud speaker is placed about one-third of a segment from a node and operated, striae begin to form on either side of the dust piles and move toward the antinodes. The first stria to reach the midpoint of a given segment stops and the next one coming up approaches within a certain distance of the central one, when it too stops. The third stria approaches within a similar distance of the second and likewise stops. This is continued till the dust figures occupy perhaps eight-tenths of a segment. The extreme striae (that is, the ones nearest the nodes), in this case are decidedly concave toward the nodes and the concavity falls off gradually in going toward the antinodes. In an extreme case, the only stationary stria is the one at the middle of the antinode; all others gradually moving along the axis of the tube from the nodes toward the antinodes, the terminal ones having the more rapid motion. These

overtake the more slowly moving ones and finally unite with them. At the same time, dust is leaving the more stable striae and moving back along the walls of the tube toward the nodes. Much of this returning dust seems to move underneath the advancing striae, while the rest of it streams back higher up on the sides of the tube, above the striae. This returning dust forms new striae near the nodes, which again advance toward the antinodes. By shifting the vibrator toward an antinode, the forward motion of the striae can be greatly reduced; and when the vibrator is at the antinode, only two or three of the terminal striae show any forward motion at all. These terminal striae are now concave toward the antinodes instead of toward the nodes and the dust occupies about half as much of the segment as before. If the vibrator is moved to a node, the dust leaves the antinodal region entirely and forms striae about the nodes which are concave toward the nodes. The excitation of the dust is now a minimum and these striae exhibit no apparent forward motion at all.

The above observations, therefore, seem to lend credence to the conclusion of Dvorak,[7] based on his observations of the behavior of both liquids and dust, and to the mathematical deduction of Lord Rayleigh[8] that there is a current through the central portion of the tube from the nodes to the antinodes and a return current contiguous to the walls of the tube. It also seems quite probable that these currents have something to do with the concavity of the striae, though the case of striae concave toward the antinodes would be difficult to explain on that assumption.

The distance between successive striae of a given dust figure is not a constant. Robinson[9] found that in going from an antinode to a node the spacing gradually diminished and he succeeded in deriving an expression for this spacing distance, which he confirmed experimentally. Irons[3] attempted to verify Robinson's equation but his results failed to support it. In the present work, the spacings of many dust figures were measured and the most promising ones were used for testing Robinson's law. In no case was the agreement satisfactory. At normal atmospheric pressure, there was usually, but not always, a slight diminution in the spacing distance in going from an antinode to a node; but at pressures considerably below atmospheric, the spacing distance actually increased. It was noticed, however, that the average spacing between successive striae was much greater under some conditions than under others and an attempt was therefore made to determine the factors which exert an important influence on the spacing distance.

IV. Factors Affecting the Distance Between Striae

1. Sound intensity.

This is probably the most important factor. There are two ways in which the intensity of the sound can be varied: (a) by varying the energy input to

[7] Dvorak, Pogg Ann. **CLIII,** 102 (1874); **CLVII,** 42 (1876).
[8] Lord Rayleigh, Phil. Trans. **CLXXV,** Part I, 1 (1884) or Scient. Papers **II,** 239.
[9] J. Robinson, Phil. Mag. **18,** 180 (1909); **19,** 476 (1910).

the vibrator, (b) by shifting the position of the vibrator relative to a node. If a rod is stroked gently with the vibrator at a node, the striae will be close together, but if the rod is stroked vigorously, the striae will be few in number and much farther apart. If the vibrator is placed at an antinode, the most vigorous stroking will be required to produce a very meager spacing. An intermediate position of the vibrator will produce an intermediate spacing.

2. Size of dust particles.

This investigation failed to substantiate the work of Cook[10] who found that the spacing increased with the size of the dust particles. Minimum spacing was always obtained with medium sized particles. If either larger or smaller particles were used, the distance between striae was increased. The photographs of Fig. 2 and the curves of Fig. 3 show this very clearly. They

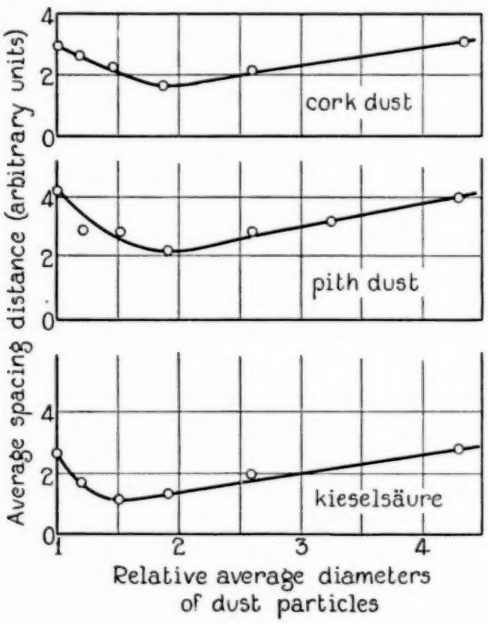

Fig. 3. Curves showing the effects of particle size on the relative separation of the striations.

also show that the size of the particle required to produce minimum spacing probably decreases as the density of the dust increases.

3. Gas pressure.

The pressure to which the gas in the tube is subjected not only affects the spacing between the striae but it also affects the number of striae in a segment, the amount of dust in each striae, and the compactness of this dust. As the pressure is reduced the striae near the nodes are the first ones to be noticeably affected. Not only do they get fewer in number and farther apart but also the particles composing them oscillate through a greater distance

[10] S. R. Cook, reference 6.

and move about with greater freedom. Thus the dust in these striae is much more greatly agitated than in the central ones. However, as the pres-

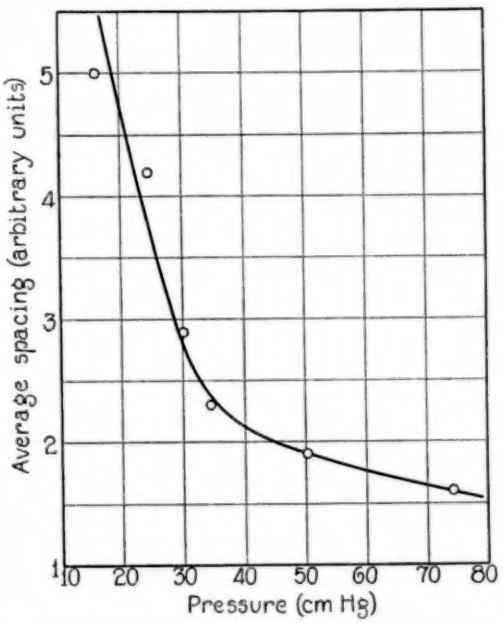

Fig. 4. Effect of gas pressure on the average distance between successive striae (pith dust, 80–100 mesh).

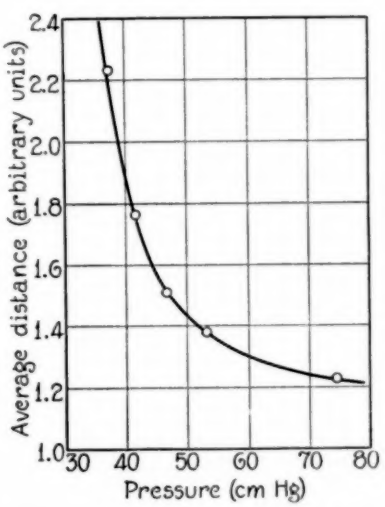

Fig. 5. Effect of gas pressure on the average distance between successive striae (cork dust, 80–100 mesh).

sure is decreased, more and more of the central striae behave in the same way till finally all are greatly agitated save the one at the middle of the segment.

With a further decrease in pressure, even this central one succumbs and behaves like the others. Finally when the pressure is reduced to 10 cm of Hg, the striae are broken up and the dust is swept from the antinodal region to the nodes. The curves of Figs. 4 and 5 show clearly that the spacing increases as the pressure decreases.

4. Density of particles.

The curves of Fig. 6 show that the density of the dust has a decided influence on the spacing between the striae so long as the density is less than 0.3

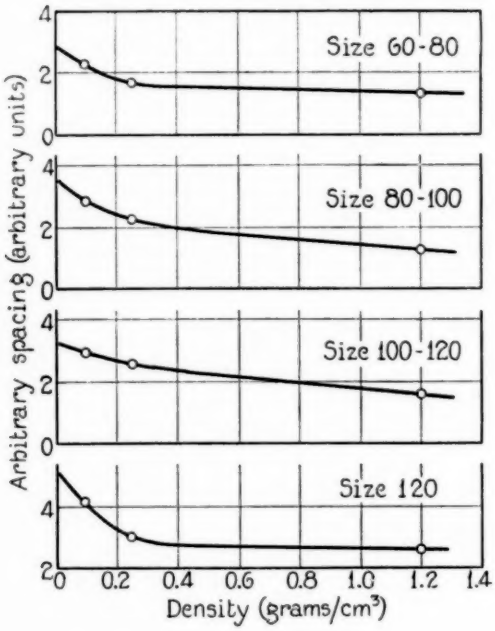

Fig. 6. Effect of density of dust material on the average distance between successive striae.

gm/cm³. Beyond 0.3, the slopes of the curves are much more gradual, but even within that range the decrease in spacing with the increase in density is sufficient to be measurable.

V. Ratio of Distance Apart of Striae to Mean Free Path of the Gas Molecules

Cook[10] worked out this ratio for amorphous silica in air. The results were not conclusive, but they were sufficient to indicate a probability that the distance apart of the striae is directly proportional to the mean free path of the gas molecules.

Similar computations were made with the data obtained in this work. The results, shown in Table I are no more conclusive than were those of Cook.

TABLE I.

Material (in all cases, 80–100 mesh)	Pressure p cm of Hg	Distance apart of striae (d) mm	Mean free path (l) cm	d/l $\times 10^{-4}$
Pith	74.5	1.6	940×10^{-5}	170
Pith	50.1	1.9	1390×10^{-5}	137
Pith	41.3	2.0	1700×10^{-5}	118
Pith	34.6	2.3	2030×10^{-5}	113
Pith	29.8	2.9	2350×10^{-5}	123
Pith	24.7	4.2	2880×10^{-5}	146
Pith	15.8	5.0	4450×10^{-5}	113
Cork	74.5	1.2	940×10^{-5}	128
Cork	53.3	1.4	1320×10^{-5}	106
Cork	46.7	1.5	1510×10^{-5}	99
Cork	41.5	1.8	1690×10^{-5}	106
Cork	37.2	2.2	2010×10^{-5}	102

VI. CONCLUSIONS

An experimental investigation of the properties of the striations in Kundt's tube dust figures was made. With a loud speaker for a source of sound, it was found that position of the vibrator which produced maximum intensity was different from that obtained when a stroked rod was used as a source. The changes in the spacing between the striations caused by altering the pressure, the size of the particles, the intensity of the sound, and the density of the particles, were investigated.

WAVE-PARTICLES AS TRANSMITTED POSSIBILITIES: QUANTUM POSTULATES DEDUCED FROM LOGICAL RELATIVITY

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(Received September 24, 1930)

Abstract

General relativity is logically unsatisfactory because it bases measurement on infinitesimals, and absolute infinitesimals do not exist. A standard of comparison being a logical necessity, we propose to provide it by the new fundamental hypothesis; "The physical world is composed of elementary events of identical and definite non-zero four-dimensional extent." The photon is a possibility of absorption-event initiated by an emission event; it is exhibited as a set of superposed moving volumes or three-dimensional sections of the four-dimensional possibility. The electron is a possibility transmitted with smaller velocities. Mass or energy is proportional to the time-duration of the event-possibilities, and obeys thence, the relativity rules. A wave function is postulated for the possibility being realized, and from Doppler's principle the quantum rule necessarily follows: mass proportional to frequency, and group-velocity equal to particle velocity. The "particle" exists only when the transmission is parallel the time-edge of the possibility; in atomic orbits presumably the condition does not apply, and the parallel-displacement tracks of relativity which are shown to to be required outside, do not apply within the atom. The finite extent of the events which exhibit the particle necessitates an indeterminacy in the situation of the particle.

§ 1. Logical Weakness of the General Theory of Relativity

IN UNIFIED field theory, particularly the form given by Eddington, tracks of all particles, and straight lines, are defined by means of infinitesimals, or infinitesimal displacements. Thus at the basis of the theory rests a set of equations of the form[1,6]

$$dA_i = (ij,\ k)A_k dx_j \cdots i, j, k = 1, 2, 3, 4.$$

The displacement dx_j is supposed to be infinitesimal, and the corresponding increment dA_i must also be infinitesimal. It is however a mathematical fact that there are no absolute infinitesimals, and that the property of being small is only relative. In applying the relativity to experience, we have to fix arbitrarily what shall be small. Thus there is nothing in the relativity theory of geodesics to say that the orbits shall not represent electron tracks round atoms rather than planetary tracks, and nothing but a pragmatic test to give the verdict. This elasticity may be satisfactory from the experimenter's point of view, but the theoretician cannot be satisfied until the theory can tell itself whether its findings are to apply to microscopic or macroscopic phenomena. Relativity at present finds that phenomena on the minute can be only a replica of phenomena on the grand scale; there is in its very fundamental constitution no absolute infinitesimal, it is the merely relative infinitesimal

[1] Eddington, Mathematical Relativity, p. 213, Eq. 91.1.

of mathematics in which any contortion of curvature may exist and which is merely a class of finites.[2]

Herein is not only a logical defect of the theory, but also the reason why the theory fails to include atomic phenomena within its unifying field. Classical physics I suppose would have unanimously supported the view that phenomena on the minute were replica of those on the large scale; but with the advent of atomic physics this attitude has died, and the principle of indeterminacy has introduced an absolute standard of minuteness into physics that is not in pure mathematics.

Thus, to give it logical completeness, relativity requires an added postulate over and above the postulates made by Einstein at the foundation of the theory. Einstein's postulates concerned with observers, the fact that all observers were on the same footing for erecting descriptions of the external world; but the new postulate must concern the means whereby the knowledge of the external world is derived by all observers. We postulate that "The observations of every observer can be analyzed into a complex of minute events each with the same four-dimensional extent." The old postulates asserted that differences between observers were only relative, while the new postulate asserts that the differences between the minute events observed are also only relative. It carries the relativity a step further into the heart of physics; and incidentally provides a standard of minuteness for relativity, raising that theory to a more completely logical status.

Other postulates, of course, suggest themselves as alternatives; for instance the postulate that space-time is itself discontinuous, or that there is a minimum quantum of action, where action is defined from the usual relativity equations. We may justify our actual choice by appealing to Whitehead's philosophy of space-time.[3] This philosophy, generally accepted by those who have taken the trouble to study it, at least in general idea, shows that space-time may be logically defined from the extensive properties of events. Thus the world of events is fundamental, and space-time comes out of it by an abstractive process actually carried through with some success by Whitehead. Thus we cannot lightly postulate a discontinous space-time after Whitehead has erected a continuous one, until someone succeeds in erecting a discontinuous one and elucidates what the meaning of such a construct really is. Again, accepting Whitehead's philosophy, we immediately see that our fundamental postulate must concern with events rather than with such entities as mass or action, or for that matter with space-time either. If there is a minimum action or mass, or a discontinuous space-time, it should come out of the theory since relativity defines mass and action from functions in space-time, and not need tacking on to the theory as an *ad hoc* assumption. The properties of space-time that give a minimum action must be derivable from the events in terms of which the space-time is defined; hence our fundamental hypothesis must concern with events.

[2] Whitehead, Process and Reality, p. 465.

[3] Whitehead, Process and Reality and Principles of Natural Knowledge.

We claim therefore that our postulate is logically required to make the theory satisfactory at its foundation, and does not add anything *ad hoc* to the after structure of the theory.

§ 2. Geometry of Four-Dimensional Regions

We propose to examine the representation of minute four-dimensional regions representing the minimum events of the world on the Minkowksi diagram. In drawing Minkowski diagrams the beginner generally has to remind himself that a point on the diagram represents a definite and unalterable event with definite coordinates in both space and time for each system concerned. But in representing the minute events postulated here on a scale that shows the boundaries of the events as lines in the diagram, we can no longer assume that each point on the diagram represents a definite event for every system; there are no events of such precise coordinates. This lends a certain elasticity to the diagrams that is not familiar, and that must be carefully remembered in following the argument given below; the same event may be represented, if convenience dictates it, by differently shaped areas in the different systems of reference.

In some particular system S' the simplest four-dimensional region is a volume stationary and existent for a definite time; suppose it represented by $AB'CD'$ where AB' is along X' axis, and AC along T' axis, giving a two-dimensional section. We shall suppose that the same event is in a system S represented by $ABCD$ where $B'D'$ cuts the X axis in B; this will be a moving volume, for S, existent for a definite time.

Let dt, dt' be the time durations of the event, and dV, dV' the two volumes proportional to the X, X' sections. Then simple relativity transformations show that, taking velocity of light unity for convenience,

$$dt' = (1 - v \cdot v)^{1/2} \cdot dt; dV' = dV \cdot (1 - v.v)^{-1/2}: \tag{1}$$

where v is the velocity of S' relative to S. Thus the four-dimensional extent $dt \cdot dV = dt' \cdot dV'$ is a constant or invariant for this transformation.

In the particular case when v is unity, these formulae are no longer of use, for there are no systems S, S' with this relative velocity. If we call the velocity given by the gradient of the edge AC of the event the "self-velocity" of the event, then there may be events with self-velocity unity but which can therefore never be exhibited as volumes stationary in any coordinate system. Such an event could be represented by $ABCD$ for S, where AC is along the light-track gradient unity, and AB along the X axis. This would transform to $AB'CD'$ for S' with C still on the light track and B' at the intersect of BD with the X' axis. Here we can easily see that

$$dV' = dV(1 + v)/(1 - v \cdot v)^{1/2} \tag{2}$$

$$dt' = dt(1 - v \cdot v)^{1/2}/(1 + v) \tag{3}$$

and again the four-dimensional extent of the event is invariant. Alternatively the formulae may be written

$$dV = dV'(1 - v)/(1 - v\cdot v)^{1/2} \tag{2'}$$

$$dt = dt'(1 + v)/(1 - v\cdot v)^{1/2} \tag{3'}$$

with

$$dt = k/dV,\ dt' = k/dV'. \tag{4}$$

These of course hold only when the self-velocity of the event is parallel the relative velocity of S, S'. If the relative velocity v is along the Y, Y' axes, and the self velocity of the event is along the X, axis, then by drawing the appropriate figure it can easily be verified that

$$dt' = dt/(1 - v\cdot v)^{1/2} \tag{5}$$

$$dV' = dV(1 - v\cdot v)^{1/2} \tag{6}$$

with again

$$dt' = k/dV',\ dt = k/dV; \tag{4'}$$

the most general case being easily deducible from these two.

§ 3. Transmission of Four-Dimensional Regions

(a). Regions with unit self-velocity. Photon theory.

Suppose that the region $ABCD$ of the previous article represents one stage in the process of transmission of a possible event, the transmission being with the same vector velocity as the self-velocity of the possible event. The region $ABCD$ is a section (X-axis) of the region that would be occupied by the event were it to be realized at that stage, and examined by the system S. The fact that it is being transmitted along the X-axis means that the boundary AB is moving along the X-axis with the velocity of transmission, and the boundary CD is also moving along the X-axis with the same velocity. Since this velocity is the same as the velocity given by AC or BD we see that the boundary AB reaches the stage CD after the time dt which is the duration of the possible event. Thus in the realized event CD is ahead in space, but behind in time compared with AB, but in the transmission AB and CD coincide, for the occurrence of CD is simultaneous with the arrival of the transmitted AB. Were the transmission to materialize into an event, the edge AB would be realized first, and leave the edge CD travelling on for the time dt before it was realized.

Thus the transmission looks like a simple moving volume travelling with the velocity of light; all the volumes which would occur in succession in the event appear as coincident in an instantaneous picture of the transmission, and if we had not started from the complex, we should have mistaken the process for a simple moving volume, albeit with something corresponding with a pseudo-density of the overlapping volumes.

To picture a region that has extension in space and in time that is itself being propagated with velocity through space, is a new and perhaps rather difficult concept, and the results of investigating it in detail seem to be of considerable interest.

Thus suppose that a quantum emission corresponds to a four-dimensional event with self-velocity unity, and that this originates a possible absorption transmitted with this self-velocity. This transmission will appear as a moving volume, or particle; in other words it is the photon of recent optical theory. But the photon and the transmitted possibility both differ from mere moving volumes: the one in having mass or energy, and the other in having the pseudo-density of the superposed volumes corresponding to different stages of the possible event. Identifying these differences we assume next that the energy of the photon is proportional to the time-duration of the possible event; this may be taken as a definition of the energy of a particle on the new theory.

$$E \text{ is } prop. \text{ to } dt$$

and hence from Eq. (3′)

$$E = E'(1 + v)/(1 - v \cdot v)^{1/2} \tag{8}$$

if E is the energy of the photon for S, and E' for S'.

The probability that the event will occur or that the possibility will be realized cannot be deduced *a priori;* but since the wave-theory of radiation has been interpreted statistically, we may assume that there will be a probability wave-function whose phase-velocity equals the velocity of transmission. From wave theory it then follows that in transforming between the frequencies, the generalized Doppler principle[4] will necessarily hold:

$$n = n'(1 + v)/(1 - v \cdot v)^{1/2} \tag{8′}$$

and comparison with Eq. (8) therefore shows that

$$E = hn \tag{9}$$

where h is a universal constant, the quantum theory rule. Eq. (4) shows that the volume dV is proportional to the period, and thence the wave-length of the waves; or the section of the volume in the direction of the transmission is proportional to the wave-length.

(b). Regions with any self-velocity. Electron theory.

From the results of the foregoing we are naturally lead to expect transmitted possibilities of normal velocities to have the same properties as material particles. Let an event possibility of self-velocity u be transmitted with that velocity, then the energy of the particle it appears as, is again defined as proportional to the time dt of the event-possibility, or the pseudo-density of the superposed volumes. Eqs. (1) then give

$$E' = E(1 - v \cdot v)^{1/2} \tag{10}$$

which is the usual relativity form for the energy, since here E' is the rest-energy of the particle. Translated into the usual notation it is of course

[4] Cunningham, Principle of Relativity.

$$mc^2 = m_0c^2(1 - v^2/c^2)^{-1/2}. \tag{10'}$$

If it is questioned whether the electron is but a transmitted possibility, we may point to the usual interpretation of the matrix mechanics; the electron connects quantum events, and is in effect a transmitted possibility of an absorption. From this point of view it is natural to seek for a wave-function that shall give the probability of the event being realized at any stage. But to obtain the frequency transformation of these waves we must pursue a slightly different track from that which gave us the formulae for light waves; here the velocity is not an invariant and the problem is less simple. The familiar reasoning[5] is however perfectly satisfactory and conclusive. A stationary particle must correspond with a stationary wave system, say of the form for S',

$$P = A \exp(2\pi n' i t'). \tag{11}$$

The Lorentz transformation gives

$$P = A \exp(2\pi n i t - x/w) \tag{12}$$

relative to the S system, where

$$n = n'(1 - v^2/c^2)^{-1/2} \tag{14a}$$

and

$$w = c^2/u. \tag{14b}$$

Comparison of Eq. (14a) with Eq. (10) again gives the quantum rule

$$E = hn \tag{9}$$

while combination of Eqs. (14a), (14b) shows in the usual way that u is the group velocity of the waves.

We thus reach a satisfactory interpretation of the wave theory of matter, of the nature of the electron, and the similarity, yet difference between the photon and the material particle.

§ 4. Equations of Motion of Particles

At the outset of this work we made the simplifying assumption that the transmission of the possibilities was parallel to the self-velocity of the event-possibility transmitted. Only with this assumption is the transmission exhibited as a particle, for only then will the various volume-sections of the event be superposed on one-another. When therefore the particle exists, their tracks are necessarily given by parallel displacement; for by our assumption the edges AC, CC' of consecutive possible events are parallel, and hence the edge, which is parallel to the velocity vector of the particle, is moved by parallel displacement. This leads immediately to the unified field theory already given mathematical expression by the present writer[6]; the most general

[5] Haas, Wave Mechanics and New Quantum Theory, Chap. 2.
[6] Band, Phys. Rev. **36**, 1405 (1930).

rule for the parallel displacement of the velocity vector gives the tracks of the particles actually agreeing with the experimental tracks. The small displacements of the theory must obviously be of the same order as the dimensions of the events, and the equations will be meaningless if we attempt to apply them to smaller orders of length.

But we have already seen that the existence of the particle is by no means a necessity; so far as our theory is concerned, there may be transmissions in directions other than the self-velocity of the events, and what we may vaguely call the track of the transmission will then have appreciable curvature within the extent of one possible event, and the parallel displacement rule no longer applies. These "tracks" are not then tracks of particles at all, and the usual wave-theory interpretation of quantized orbits seems to be the most natural one here.

In passing, we remark that on the present theory we have refused to regard the particle as fundamental; the whole structure of relativity is erected from events of finite four-dimensional extent, and a particle is an abstract or recognized permanency among the extensive relations between events. Thus our postulate of finite extent to the ultimate events at once forbids the accurate estimation of the position or motion of the particle when it actually exists; for the particle can only be observed through the events which exhibit it, and these do not give exactitude.

In conclusion, we cannot claim to have treated more than an elementary set of cases; but it seems sufficient to show that it is possible by recognizing a logical weakness of Relativity to deduce from the most natural additional hypothesis to remove this weakness, the essential basis of the new quantum theory; to illuminate the meaning of and deduce the assumptions of the unified field theory; and finally to suggest an interpretation of the physical world that will harmonize the two great fields of theoretical research of recent years, relativity, and atomic physics.

THE GENERAL EQUATIONS OF ENERGY AND ENTROPY OF GASES

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(Received March 9, 1931)

Abstract

By substituting the general equation of state for any gas, $p = T\Psi(v) - \Phi(v) - F(v, T)$ in the thermodynamic equation, $Tds = du + pdv$, and by applying the principle of exact differential, the following general equations of energy and entropy have been obtained,

$$u = \int \Phi(v)dv + \int \left[F - T\,\partial F/\partial T \right] dv + \alpha(T)$$

$$s = \int \Psi(v)dv - \int \partial F/\partial T\, dv + \beta(T).$$

The values of $\alpha(T)$ and $\beta(T)$, both arbitrary functions of temperature, are found to be

$$\alpha(T) = \int c_{v\infty} dT + k_1,$$

$$\beta(T) = \int \frac{\alpha'(T)}{T} dT + \text{const} = \int c_{v\infty} \frac{dT}{T} + k_2,$$

where $c_{v\infty}$ = heat capacity of the gas at constant volume and at infinite dilution. The equations are applied to a perfect gas as well as to gases obeying van der Waals', Clausius' and Dieterici's equation of state and are found to give results in agreement with those obtained from other thermodynamic equations.

PHILLIPS,[1] by employing the characteristics of exact differentials, showed that both the energy and entropy of a fluid are the sum of a function of volume and a function of temperature, if its equation of state belongs to the type,

$$p = T\Psi(v) - \Phi(v), \tag{1}$$

in which p is the pressure, T the temperature of the fluid, $\Psi(v)$ and $\Phi(v)$ are functions of volume. Eq. (1), however, is not general enough. Beattie and Bridgeman[2] pointed out that practically all the equations of state can be generalized in the form

$$p = T\Psi(v) - \Phi(v) - F(v, T) \tag{2}$$

where $F(v, T)$ is a function of volume and temperature. The purpose of the present paper is to find the general equations of energy and entropy of any

[1] Phillips, Jour. Math. and Phys., M.I.T. **1**, 42 (1921).
[2] Beattie and Bridgeman, Proc. Am. Art. Sci. **63**, 231 (1928).

fluid belonging to type (2), and the method of derivation is essentially an extension of that of Phillips.

Energy Equation

From thermodynamics we have

$$Tds = du + pdv \tag{3}$$

in which u and s are the energy and entropy of the substance. Combining with Eq. (2) we get

$$\frac{du}{T} - ds + \Psi(v)dv - \frac{\Phi(v) + F}{T} \cdot dv = 0 \tag{4}$$

where $F = F(v, T)$ for short.

As the result of straightforward calculation we have finally

$$u = \int \Phi(v)dv + \int \left[F - T\frac{\partial F}{\partial T}\right]dv + \alpha(T). \tag{5}$$

Entropy Equation

By combining Eqs. (2) and (3), we get

$$du - Tds + [T\Psi(v) - \Phi(v) - F]dv = 0. \tag{6}$$

Proceeding as before, we find

$$s = \int \Psi(v)dv - \int \frac{\partial F}{\partial T}\, dv + \beta(T). \tag{7}$$

Determination of $\alpha(T)$ and $\beta(T)$

The relation between $\alpha(T)$ in Eq. (5) and $\beta(T)$ in Eq. (7) can be easily derived. From Eqs. (5) and (7) we get

$$du = \left[\Phi(v) + F - T\frac{\partial F}{\partial T}\right]dv - \left[\int T\frac{\partial^2 F}{\partial T^2}\, dv - \alpha'(T)\right]dT \tag{8}$$

$$ds = \left[\Psi(v) - \frac{\partial F}{\partial T}\right]dv - \left[\int \frac{\partial^2 F}{\partial T^2}\, dv - \beta'(T)\right]dT. \tag{9}$$

Substituting these values of du and ds and that of p in Eq. (2) in Eq. (3) and collecting terms, we get

$$T\beta'(T) = \alpha'(T) \tag{10}$$

or

$$\beta(T) = \int \frac{\alpha'(T)}{T}\, dT + \text{const.} \tag{11}$$

In the determination of $\alpha(T)$, the energy equation presents no difficulty, but in the case of $\beta(T)$, the integral of the entropy equation becomes infinite at the lower limit because of the presence of a term $\ln v$ or $\ln(v-b)$. In the pres-

ent method $\alpha(T)$ is evaluated from the initial condition, while $\beta(T)$ is found from Eq. (29). A common method[3] of finding $\alpha(T)$ is to assume that at infinite dilution (i.e., $v \doteq \infty$) the gas approaches the perfect state

$$u_{v=\infty} = \alpha(T) = \int c_{v=\infty} dT + k_1 \tag{12}$$

and Eq. (11) gives

$$\beta(T) = \int c_{v\infty} \frac{dT}{T} + k_2 \tag{13}$$

where $c_{v\infty}$ is the heat capacity of the gas at constant volume and at infinite dilution, and k_1 and k_2 are arbitrary constants.

Application to Some Equations of State

1. Perfect gas:

$$p = \frac{RT}{v}.$$

Referring to Eq. (2), we see

$$\Psi(v) = \frac{R}{v}, \quad \Phi(v) = 0, \quad F(v, T) = 0.$$

Eqs. (5), (7), (12), and (13) give

$$u = \alpha(T) = c_v T + k_1$$
$$s = R \ln v + c_v \ln T + k_2$$

in which $c_v = c_{v\infty}$ for perfect gas.

2. van der Waals' equation:

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Here

$$\Psi(v) = \frac{R}{v - b}, \quad \Phi(v) = \frac{a}{v^2} \quad F(v, T) = 0.$$

Assuming $c_{v\infty}$ to be independent of temperature, Eqs. (5), (7), (12), and (13) give

$$u = -\frac{a}{v} + c_{v\infty} T + k_1$$

$$s = R \ln (v - b) + c_{v\infty} \ln T + k_2.$$

3. Clausius' equation[4]

$$p = \frac{RT}{v - a} - \frac{c}{T(v + b)^2}.$$

[3] See, for instance Schaefer, Einführung in die Theoretische Physik, Walter de Gruyter and Co., Berlin, 1929, Band II p. 189; van der Waals-Kohnstamm, Lehrbuch der Thermodynamik, Verlag von Johann Ambrosius Barth, Leipzig, 1908, 1. Teil, p. 44.

Here

$$\Psi(v) = \frac{R}{v - a}, \quad \Phi(v) = 0, \quad F(v, T) = \frac{c}{T(v + b)^2}.$$

The same set of equations gives

$$u = -\frac{2c}{T(v + b)} + \int c_{v\infty} dT + k_1$$

$$s = R \ln (v - a) - \frac{c}{T^2(v + b)} + \int \frac{c_{v\infty} dT}{T} + k_2.$$

4. Dieterici's equation[5]

$$p = \frac{RT}{v - b} e^{-a/vRT}$$

which, on expansion, becomes

$$p = \frac{RT}{v - b} - \frac{a}{v(v - b)} + \frac{a^2}{2RTv^2(v - b)} + \cdots.$$

Taking only the first three terms and referring to Eq. (2) we find

$$\Psi(v) = \frac{R}{v - b}, \quad \Phi(v) = \frac{a}{v(v - b)}, \quad F(v, T) = \frac{-a^2}{2RTv^2(v - b)}$$

Eqs. (5), (7), (12), and (13) give

$$u = \left[\frac{a}{b} - \frac{a^2}{b^2RT}\right] \ln \frac{v - b}{v} - \frac{a^2}{bRTv} + \int c_{v\infty} dT + k_1$$

$$s = R \ln (v - b) - \frac{a^2}{2b^2RT^2} \ln \frac{v - b}{v} - \frac{a^2}{2bRT^2v} + \int \frac{c_{v\infty} dT}{T} + k_2.$$

The above results are checked by integrating the following thermodynamic equations, after substitution of the values of $(\partial p/\partial T)_v$ and p in each equation of state

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

Eqs. (5) and (7) can be applied to any other equation of state, but the above examples are sufficient to show their usefulness.

Dr. D. Sun of the Department of Mathematics gave most valuable as sistance for which the author is grateful.

[4] Clausius, Wied. Ann. **9,** 337 (1880).
[5] Dieterici, Wied. Ann. **69,** 685 (1899).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Aluminum May Have A Nuclear Spin

In a recent letter to the editor of the Physical Review, R. C. Gibbs and P. G. Kruger, (Phys. Rev. **37,** 656 (1931)) report a negative result in their search for hyperfine structure in the arc and first spark spectrum of aluminum. Due to the importance of this result it should be pointed out that the evidence is not conclusive and that aluminum may have and is predicted to have a nuclear spin.

The arc lines investigated involving the transitions $^2P_{1\frac{1}{2},\frac{1}{2}}(3p)-{}^2S_{\frac{1}{2}}(4s)$ would not be expected to give very large *hfs* separations since the penetrating electron is a somewhat loosely bound 4*s* and not a tightly bound 3*s* electron. One would expect very narrow *hfs* for both the ^2P and ^2S terms.

In the first spark spectrum of aluminum, Al II, a 3*s* electron is involved in both the initial and final states of the lines investigated. The hyperfine structure separations of the $^3D_3(3s4d)$ term and the $^3F_4(3s9f)$ term should, due chiefly to the 3*s* electron, be large, normal, and almost identical in separation. The result is that the strong *diagonal lines* should fall together and give a strong sharp line and the faint *off diagonal lines* not be observed. Using a nuclear spin of 3/2 the *diagonal components* of 4226 ($^3D_3-{}^3P_4$) should have a total intensity sixteen times that of the *off diagonal components*. A very similar known case is 4823, $^5P_{4\frac{1}{2}}-{}^5S_{3\frac{1}{2}}(3d^54s4p-3d^54s5s)$ of manganese, (White and Ritschl, Phys. Rev. **35,** 1155 (1930)), in which the six diagonal lines fall close together, the term separations being due chiefly to the tightly bound and penetrating electron 4*s*. The same should be true for the $^1D_2(3s3d)$ and $^1P_1(4s4p)$ term except that here the wide *hfs* terms should be inverted. The strong *diagonal lines* should again fall together and give a fairly sharp line.

A better test than the one chosen would be combinations between levels having widely different separations, e.g. the *off diagonal multiplet lines* $^3D_3-{}^3F_3$ or $^3D_2-{}^3F_2$ ($3smd-3smf$). The $^3D_2$ and $^3F_3$ terms should have very narrow separations and the $^3D_1$ and $^3F_2$ terms should have *inverted* but rather wide separations.

H. E. WHITE

University of California,
Berkeley, California,
April 20, 1931.

The Fundamental Assumptions in Akulov's Papers on Ferromagnetism

In a series of papers[1] Akulov has developed a mathematical theory capable of quantitatively describing a good many ferromagnetic phenomena. The success of his work is some what marred by two fundamental assumptions: (1) That ferromagnetic atoms in a crystal have quadrupole moments. (2) That the Weiss-Heisenberg theory is incorrect (spontaneous magnetization in zero field does not exist).

It is the purpose of this note to point out that these assumptions are arbitrary only in their wording, and that their physical content may be retained without having to assume any new or unexplained physical processes.

As to the first point, quadrupole moments are assumed in order to account for the fact that I and H are not, in general, parallel in a cubic crystal. Heisenberg has suggested[2]

[1] N. S. Akulov, Zeits. f. Physik **67,** 794, (1931). References to previous articles are given in this paper.

[2] W. Heisenberg, Metallwirtschaft **9,** 843, (1930).

that this is due to a coupling between spin and orbital moments. The idea has been carried out mathematically by Powell[3] who obtains essentially the same formulae as Akulov for the dependence of the energy on the direction of magnetization. In other words, one might express Powell's result by saying that, by taking into account the interactions of the type $(s-l)$ a ferromagnetic lattice is in certain respects equivalent to a lattice of quadrupoles.

Secondly, to account for the low hysteresis in single crystals, Akulov finds it necessary to assume that there are no regions of spontaneous magnetization. In one of his papers he has what purports to be a proof of the impossibility of spontaneous magnetization.[4] That this proof is not valid is evident from the argument in the ensuing communication. It *is* possible to have spontaneous magnetization in various regions and at the same time negligible hysteresis losses, provided the regions are sufficiently small. In other words, by assuming the regions of spontaneous magnetization to be small, it is possible to satisfy Akulov's assumption of demagnetization (Schrumpfprozess) in a single grain without destroying the Weiss-Heisenberg theory.

FRANCIS BITTER
Westinghouse Research Laboratories,
East Pittsburgh, Pennsylvania,
March 30, 1931.

[3] F. C. Powell, Proc. Roy. Soc. **A130,** 167 (1930).

[4] N. S. Akulov, Zeits. f. Physik **64,** 559 (1930).

Block Structure and Hysteresis Phenomena

In a previous communication[1] I have pointed out the possibility that the regions of spontaneous magnetization in the Weiss-Heisenberg theory are very small, containing very roughly 10^6 atoms, and that perhaps they are related to Zwicky's block structure.[2] Since then it has been possible to make some of the calculations more precise. The details will be published elsewhere. At present I wish to point out how a magnetization curve is to be described. Consider a single crystal made up of blocks and let the energy per block be given by an expression,[3] for instance, of the type

$$\Phi = A + B\cos(\theta+\alpha) + C\cos 2\theta + D\cos 4\theta$$

The above expression for Φ is written in this form to indicate, first, a dependence on the orientation of the magnetization with respect to the crystal axes, and secondly, the existence of several minima for Φ. The depth and position of these minima depend on the values of A,B,C,D, which, in turn, depend on constants of the material, on the internal strains, and on the applied magnetic field. For equilibrium, the probability of finding a block magnetized in the direction θ is given by an expression of the form $\exp(-\Phi/KT)$. If the depth of the minima of Φ is large compared to KT, the directions of magnetization will be almost entirely confined to these minima, and a transition from one minimum to another will be very improbable. This gives rise to hysteresis and magnetic viscosity. The procedure for handling this problem is being presented at the Washington meeting of the American Physical Society. If, however, the depth of the minima is of the same order of magnitude as KT, transitions from one minimum to another are reasonably probable, and we have, practically, the above exponential distribution at all times. Thus, to state the case crudely, if the shape of the potential Φ is slowly varied by varying H, the resulting intensity will be independent of the previous history of the sample provided the depth of the minima of Φ is of the same order of magnitude as KT. Akulov[4] estimates the depth of the minima in unstrained single crystals of iron to be 10^5 ergs/cm^3, and points out that the hysteresis of single crystals is negligible, That is, I is independent of the previous history of the sample. Then, according to the above, if v is the volume of a block, we must have

$$\Phi \sim v\times 10^5 \text{ ergs/cm}^3 \sim KT = 1.37\times 10^{-16}\times 300$$
$$v \sim 4\times 10^{-19} \text{ cm}^3.$$

[1] F. Bitter, Phys. Rev. **37,** 91, (1931).

[2] D. Zwicky, Helvetica Physica Acta **3,** 269 (1930).

[3] N. S. Akulov, Zeits. f. Physik, **67,** 794, (1931); F. C. Powell, Proc. Roy. Soc. **A130,** 167, (1930); R. Becker, Zeits. f. Physik **62,** 253, (1930).

[4] N. S. Akulov, Zeits. f. Physik **64,** 559 (1930).

If v_0 is the average volume per atom, and $n = v/v_0$ = the number of atoms per block, we have that $v_0 = M/N\rho = 56/6 \times 10^{23} \times 8 = 1.2 \times 10^{-23}$ cm³ and hence $nv4 \times 10^{-19}/1.2 \times 10^{-23} =$ 35,000 atoms or roughly the same number as that previously deduced.

FRANCIS BITTER
Westinghouse Research Laboratories,
East Pittsburgh, Pennsylvania,
March 30, 1931.

Electron-pair Bonds versus Polarization in Crystals

In a letter in the March 15th number of the Physical Review (**37,** 775 (1931)) Mr. W. H. Zachariasen states, "So far the application of the principles of shared electron pairs on the atomic arrangement in inorganic crystals has proved unsuccessful, while considerations of the crystal structure from point of view of ions, ionic dimensions, ionic polarizability, and crystal energy . . . have given very valuable and important results." Such a statement I can hardly let go unchallenged.

Certainly the concepts of ions, ionic dimensions and crystal energy have proven very useful, especially in the theoretical treatment of such structures as the alkali halides, in which without question the structural units are simple ions. That however does not justify the consideration of XO_3^- ions as composed of O^{--} and distorted X^{+5} ions, when much chemical and physical evidence points to the existence of non-polar bonds between the atoms in such groups. We can agree that polarization does exist in an ion of this sort, but it seems to me more logical to consider it a *result* of the fact that completion of the valence shells of all these electronegative atoms by the formation of shared electron-pair bonds produces an unsymmetrical arrangement, rather than the *cause* of that arrangement.

The polarization concept has been used to "explain" many things[1] which are probably little related to it,—for instance the irregularities in melting and boiling points of the alkali halides, later given a satisfactory quantitative treatment by Pauling[2] on the basis of "radius ratios." On the other hand the Lewis theory of shared electron-pairs is now generally agreed to for molecules and for ions (including XO_3^-)in solution and I see no reason why it should not apply equally well to crystals. One can predict from it in the first place whether or not any electronegative atoms will be adjacent to each other in the crystal and in the second place not only the number of "contacts" between electronegative atoms but also the approximate angles between them. How else can one explain such structures as those of I_2, Se, Te, As, Sb, Bi, FeS_2, SiO_2, As_4O_6, $K_2S_2O_6$[3] (in which pairs of sulfur atoms are surrounded at corners of a distorted octahedron by oxygen atoms), and many more? I can imagine no satisfactory explanation in terms of "ions, ionic dimensions, ionic polarizability and crystal energy"alone. The "tetrahedral" XO_3^- structure, indicated in the early work on $NaClO_3$ and $NaBrO_3$ and beautifully proven by Mr. Zachariasen's researches, furnishes still another example of a prediction directly from Lewis' postulates which has been experimentally verified.

Mr. Zachariasen states that "Until one is able to treat the quantization of the electrons in polyatomic groups completely on the basis of wave mechanics, we must be satisfied with rough approximations." In view of Pauling's recent very satisfactory wave-mechanics treatment of electron-pair bonds in crystals[4] perhaps he will now be willing to abandon his rough approximations in favor of the point of view I have been upholding.

In order that there be no misunderstanding regarding the rule given in the next to the last paragraph of Mr. Zachariasen's communication, I might mention that for every example given the predictions on the basis of the Lewis theory would be precisely the same. Moreover Lewis' conceptions are much more general in their application than is this rule and so more useful.

Perhaps after I have read Mr. Zachariasen's

[1] For a summary see Grimm, Handbuch der Physik **24,** 561–568 (Springer, Berlin, 1927(.

[2] Pauling, Zeits. f. Krist. **67,** 377 (1928).

[3] The analysis of this structure, by Glenn O. Frank and the writer, was reported at the Toronto Meeting of the Mineralogical Society of America last December and will soon be submitted for publication in the American Mineralogist.

[4] Pauling, J. Am. Chem. Soc., April 1931; also in a forthcoming article in the Zeitschrift für Kristallographie.

forthcoming article on XO_3 groups in crystals (which I shall be much interested in doing) and he has read one of mine on "Principles Determining the Arrangement of Atoms and Ions in Crystals," to be published soon in the Journal of Physical Chemistry, as well as the articles of Pauling's mentioned, we can come to a better mutual understanding.

MAURICE L. HUGGINS
Stanford University,
Stanford, California,
April 9, 1931.

Evidence of the Detection of Element 85 in Certain Substances

With a magneto-optic method of analysis (Allison and Murphy, Jour. Amer. Chem. Soc. **52,** 3796 (1930); Phys. Rev. **36,** 1097 (1930)) we have made a search for element 85 in various substances in which its presence might be suspected. Out of a considerable number of substances examined, we have found evidence which seems to us to indicate, to a high order of probability, the presence of element 85 in the following: sea water, fluorite, apatite, monazite sand (Brazilian), kainite (Stassfurt), potassium bromide, hydrofluoric acid and hydrobromic acid. The evidence is presented in the data displayed in the accompanying graphs, and is supported by certain chemical reactions.

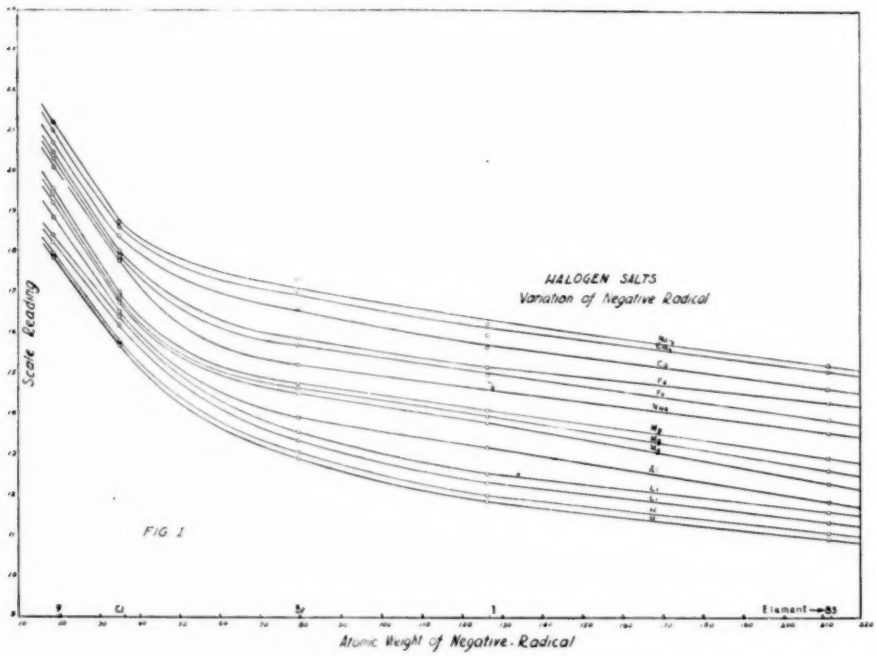

Fig. 1.

In Fig. 1 are plotted the atomic weights of the halogens against the scale readings of the minima of light intensity characteristic of several of their compounds, increasing scale readings representing decreasing time lags. These acids as do other inorganic acids which we have studied, produce each two characteristic minima, while the salts, as do other inorganic salts, produce in general minima equal in number to the known isotopes of the metallic element of the salt.

The two lower curves (Fig. 1) show our observations for hydrofluoric, hydrochloric, hydrobromic, hydriodic acids and what we will call provisionally "85" acid, each acid forming two minima of light. The other curves, in order, exhibit the data obtained for the halides of lithium, aluminum, magnesium, ammonium, iron, calcium, and sodium. It will be seen that we find minima in each case appropriate to an "85" salt, that the number of these minima is without exception

the same as that of the other halides and that they lie well on the extended curves.

The same data are shown somewhat differently in Fig. 2, in which the chemical equivalents of the isotopes of the metallic radicals

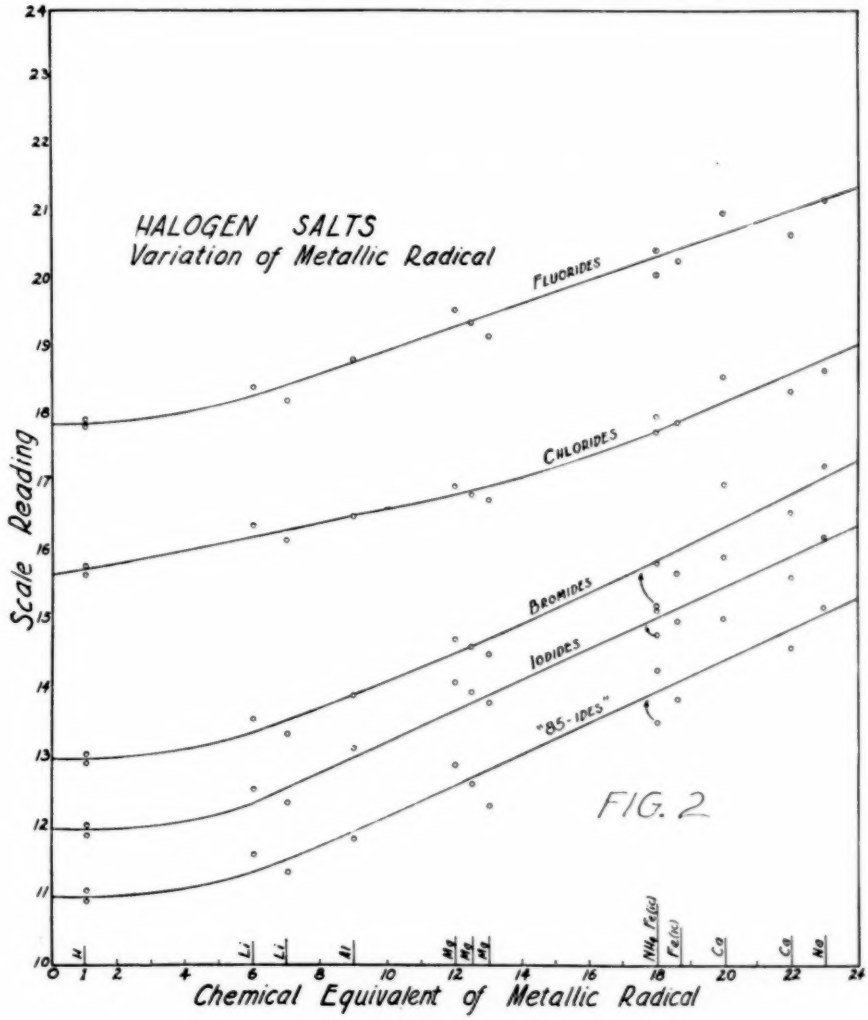

Fig. 2.

are plotted against the scale readings of the characteristic minima of the compounds. The upper curve represents the fluorides of hydrogen, lithium, aluminum, magnesium, ammonium, iron, calcium and sodium. The next three curves represent, respectively, the chlorides, the bromides and the iodides, while the last curve represents what we have termed the "85"-ides, of the same elements. We have not as yet extended our observations for the five series beyond sodium, except in the case of the chlorides, because of the difficulties introduced by the overlapping in these regions of the scale of the minima produced by the halogen salts of the heavier elements.

According to our quantitative estimates, the greatest abundance of the element found in any of the above mentioned substances, in unconcentrated form, is of the order of 1 part in 10.[9] Concentrations in the form of Li85, using monazite sand as a source, are now in progress and have already met with considerable success. The characteristic minima of H85 disappear on the addition of aqua regia, bromine or iodine to the solution. These

minima are restored by the addition of sulphur dioxide or stannous chloride. These are the only oxidizing and reducing agents which have been tried. All reagents used gave negative tests for H85.

These investigations have been under way since the middle of the past summer. More recently they have been repeated and extended by one of us (F.A.) in a somewhat more precise manner, while the chemical investigations have been carried on by two of us (E.R.B. and A.L.S.).

FRED ALLISON
EDGAR J. MURPHY
EDNA R. BISHOP
ANNA L. SOMMER

Department of Physics,
Alabama Polytechnic Institute,
April 3, 1931.

The Principle of Continuity and Regularity of Series of Atom Nuclei (Atomic Species)

While what may now be called the principle of continuity and regularity of the series of atomic species, has been used by the writer in the prediction of isotopes, and has been presented in the form of diagrams for 10 years, the complexity of the diagrams seems to have prevented the recognition of this principle by others. It therefore seems important to give a name to the principle and to illustrate it by simple drawings.

The first figure is taken, with five minor changes which do not affect the general pattern, from a diagram of the helium-thorium series which was used to predict numerous isotopes, most of which have now been found or shown to be probable. The maximum number of isobaric species given in this 1923 figure (J. Franklin Inst. **195,** 554) is 3, as is shown in Fig. 1.

The uranium series (Fig. 2) exhibits at

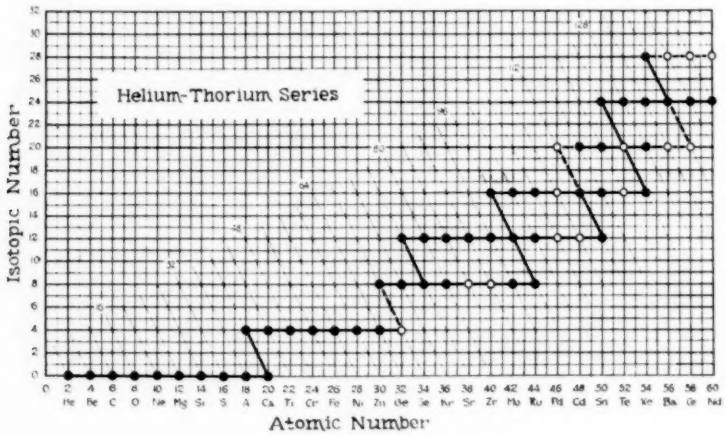

Fig. 1.

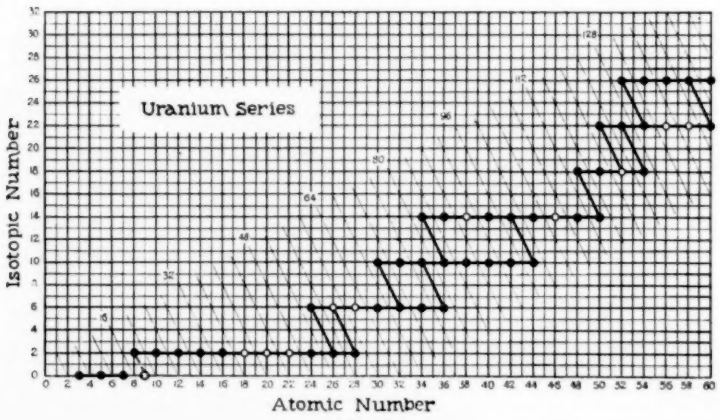

Fig. 2.

present a very simple pattern. The atomic masses (diagonal lines) for both the uranium ($4n+2$) and the thorium ($4n$) series are even, and the general increment of isotopic number or atomic mass between levels in either series is 4, which represents an increment of 2 in the number of cementing or β-electrons. Among the non-radioactive elements a single isotopic number in no case represents species of both the atomic number. The minor differences are explained by other relations presented earlier. These cannot be discussed, on account of lack of space, except that it may be stated that the fact that species of isotopic number 3 are not as yet found in the lithium series, but are found in the beryllium series, is in accord with these relations. These two series thus occupy odd isotopic lines in common, and the

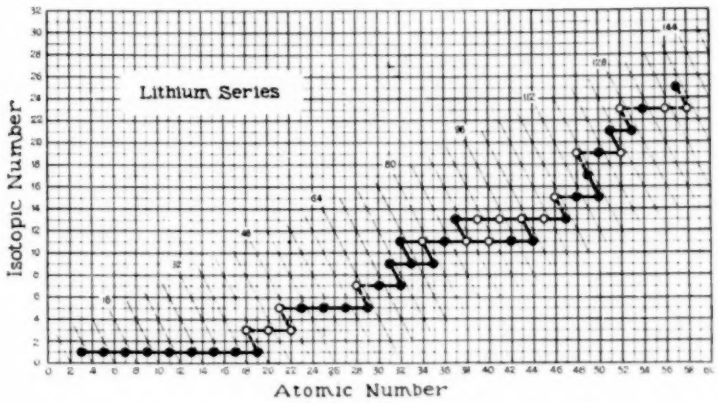

Fig. 3.

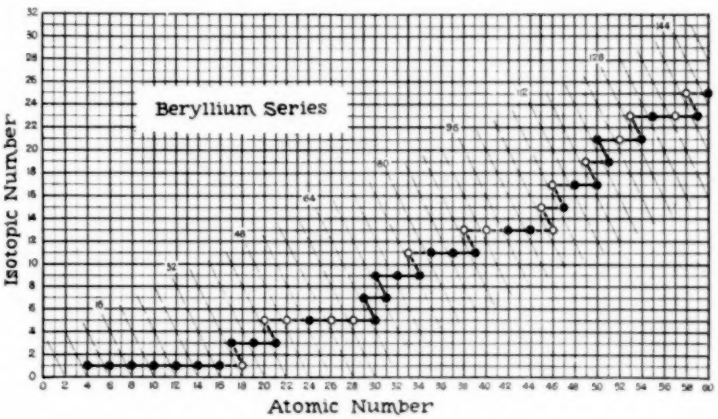

Fig. 4.

series, with the exception of three species of the uranium series on the base line, of the writer's class 4, which have the isotopic number zero, which is normally that of the helium-thorium series. Here a fluorine isotope of mass 18 is indicated as probable.

The $4n+3$ or lithium series (Fig. 3), and the $4n+1$ or beryllium series (Fig. 4) represent odd atomic weights, and the two patterns are made almost identical if the lithium series is plotted with $Z+1$ as abscissae, where Z is general increment in isotopic number in either series is 2.

If the lithium and beryllium series together are considered as a single or "odd" series, very simple relations are exhibited, or the principle of continuity and regularity still holds. Along a given isotopic line the increment of atomic number is one, of atomic mass 2, and of number of electrons, one. Thus the common increment is represented by the formula p_2e in which p represents a proton and e an electron.

This corresponds to an increment of a half alpha-particle. Thus for isotopic number 1 every atomic number from 3 to 17 represents a known species of the combined series.

The fact that the number of superposed levels in each of the even helium and uranium series is larger than in the odd lithium series is in accord with the relation (Proc. Nat. Acad. **2,** 216 (1916) and later papers) that higher nuclear stability is found in general for even than for odd nuclear charge. The smaller number of levels in the beryllium series is in accord with the even more general rule (J. Am. Chem. Soc. **39,** 859 (1917), **42,** 1991–2 (1920) that the electrons in atom nuclei are in general associated in pairs, and an odd number of electrons gives to a nucleus a relatively low stability as compared with that associated with adjacent even numbers, since the beryllium series is the only one in which the number of nuclear electrons is odd, when the atomic number is even (except the class 4 species of Li, B, and N).

The diagonal lines in the charts give the atomic masses. While chlorine of isotopic number 5 and atomic weight 39 is indicated as already discovered, the discovery is not as yet confirmed.

WILLIAM D. HARKINS

University of Chicago,
April 9, 1931.

Anomalies in Hyperfine Structures

In a recently published paper Goudsmit[1] points out that the empirically observed hyperfine structure patterns show in some cases very marked deviations from theoretically expected relationships. The discrepancy is observed in the region of high atomic numbers and is usually such as to make it necessary to ascribe an anomalously large separation to the $p_{1/2}$ term of the single electron spectrum. The interval rule appears to be obeyed in the case of Bi rather accurately. It is logical therefore to look for an explanation in the manner in which the $p_{1/2}$ and $p_{3/2}$ states interact with the nucleus.

Dirac's equation shows in fact that such a difference is to be expected. A calculation exactly similar to the one made by the writer[2] for s terms shows that $(\overline{r^{-3}})$ of the ordinary formulas for $p_{1/2}$, $p_{3/2}$ must be replaced by $(2\pi'/\Lambda)I, -(4\pi'/\Lambda)I$, $I=\int\phi_1\phi_2 r^{-3}dr$. Here ϕ_1, ϕ_2 are the two radial functions of Dirac-Gordon (denoted by Gordon as ψ_1, ψ_2). The normalizing factor is chosen so as to have $\int(\phi_1^2+\phi_2^2)dr=1$. In the neighborhood of the nucleus the "term-value energy" and screening

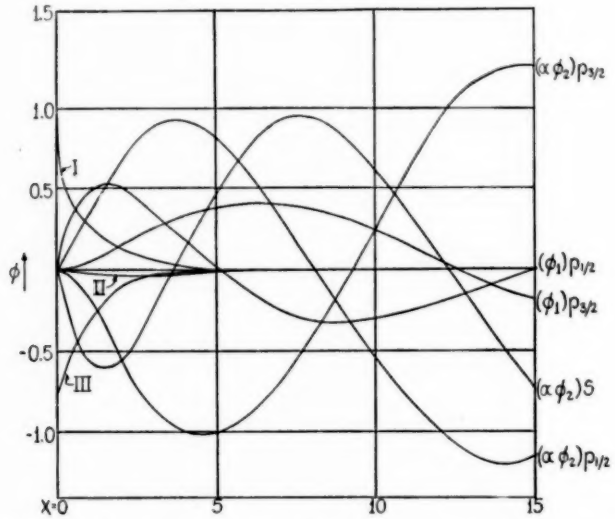

Fig. 1. I is $\phi_1\phi_2/x^2$ for $P_{\frac{1}{2}}$. II is $\phi_1\phi_2 x^2$ for $P_{3/2}$. III is $\phi_1\phi_2 x^2$ for s.

[1] S. Goudsmit, Phys. Rev. **37,** 663 (1931).
[2] G. Breit, Phys. Rev. **35,** 1447 (1930).

effects may be neglected. Under these conditions

$$\phi_1 = J_{2\rho}(2x^{1/2})$$
$$\alpha\phi_2 = (j' - \rho)J_{2\rho}(2x^{1/2}) + x^{1/2}J_{2\rho+1}(2x^{1/2})$$
$$\alpha = 2\pi Ze^2/hc,\ \rho = (j'^2 - \alpha^2)^{1/2},\ x = 2Zr/a_H$$

The J_n are Bessel functions of order n; $j' = -1$, 1, -2 for s, $p_{1/2}$, $p_{3/2}$. The results of calculation with the above formulas are represented graphically for $\alpha = 0.661$, $Z \leqq 91$. The region close to the nucleus is seen to contribute more to the I for $p_{1/2}$ than for $p_{3/2}$. The contribution to the effective value of $\overline{(r^{-3})}$ due to this region is expected to be large for $p_{1/2}$ and of the same order as the customary $2\pi\psi^2(0)$ of Fermi. In fact in the approximation of Schroedinger's non-relativistic equation we have to replace $\alpha\phi_2$ for s terms by $-x^{1/2}J_1(2x^{1/2})$. This is also plotted on the figure as $(\alpha\phi_2)_s$. The scale of all curves is seen to be roughly the same. The normalizing factor is approximately K given by $K^2(\phi_2(r)/r)^2 = 4\pi\psi^2(r)$. Hence $K^2 = 2\pi\psi^2(0)$ and $K^2 4\pi I/\Lambda \leqq 4\pi^2(a_H/\Lambda Z)\psi^2(0)\int\phi_1\phi_2 x^{-2}dx$. The integral in x is seen to be of the order of 1 and the whole of the order of $2\pi\psi^2(0)$. For comparison we have also given the $\phi_1\phi_2/x^2$ curve for s terms in the non-relativistic approximation. Dirac's equation gives higher values for s terms as well.

We may say therefore that for the calculation of the hyperfine structure intervals the $p_{1/2}$ states of heavy atoms should be considered as penetrating orbits in the neighborhood of the nucleus. For this reason alone their hyperfine structure may be anomalously great. Other effects must of course also be considered. According to Goudsmit's estimates there is no special reason to believe that they are very important. Nevertheless their effect and the contribution of regions of higher r to I must be taken into account before a quantitative comparison with experiment may be made. At present the observed deviations from simple approximate formulas are qualitatively in agreement with theory being in the correct direction and of the proper order of magnitude.

G. BREIT

Department of Physics,
New York University,
April 8, 1931.

On the Infrared Absorption by Hydrogen Sulphide at 8.0μ

Papers published by Rollefson[1] and Mischke[2] on the infrared absorption spectrum of hydrogen sulphide report the presence of an absorption band at about the wave-length 8.0μ. In a more recent paper, one of the authors working with E. F. Barker[3] at the University of Michigan, reported that a diligent search for this band had failed to confirm it. Each time when it was looked for and not found, the existence of the other two bands reported, at 2.65μ and 3.8μ respectively, were first checked. It was therefore concluded that the region at 8.0μ could not be attributed to hydrogen sulphide.

A series of measurements have been carried out with a Wadsworth prism spectrometer, especially in the region from 7.0μ to 9.0μ further to investigate the nature of the effect observed by Rollefson and Mischke. For this purpose a cell eight inches long, and equipped with rock-salt windows was used; so arranged that it could be tipped in and out of the beam. The cell was first filled with air passed through wash bottles containing KHS and then dried through towers containing successive layers of glass wool on which was sprinkled phosphorus pentoxide. A curve was first made from data taken between the dried air and the atmosphere, then a similar curve was run with the cell filled with hydrogen sulphide, purified and dried as before, and the curves were plotted for comparison. These two curves were very similar in appearance, at first glance much resembling absorption bands It was noticed, however that the ratio of the radiation apparently transmitted through the cell to that of the beam when the cell was removed (i.e. the apparent percentage absorption) was much less on the short wave side than on the long wave side. This suggested the possibility that the observed effect might be ascribed to water vapor falsification arising from the water vapor band at 6.2μ which in moist weather may well extend out beyond 8.0μ. The object of the remainder of this experiment was to test this point.

Water vapor falsifications may be very annoying, especially when long cells are used. The cell used in this experiment was equiva-

[1] A. H. Rollefson, Phys. Rev. **34**, 604 (1929).

[2] W. Mischke, Zeits. f. Physik **67**, 106 (1931).

H. H. Nielsen, and E. F. Barker, Phys. Rev. **37**, 1931.

lent to about one tenth of the entire light path. Consequently it is to be expected that in regions of water vapor absorption, when the cell, filled with very dry air, is tipped into the beam that more energy may be transmitted than when the cell is out of the beam, since by inserting the cell the path through which atmospheric water vapor absorption may occur has actually been shortened. Hence in regions of strong atmospheric absorption, one may observe what appears to be negative absorption, while in regions of less intense absorption this is less apparent or disappears entirely. These falsifications may however be quite deceiving, giving the appearance of an absorption band in the dry gas in the cell—maxima in the water vapor spectrum producing what appear to be minima in a spectrum of the gas under observation, and vice versa. To compensate for the windows, the final readings were plotted against transmission through the cell filled with atmospheric air. Curves for comparison representing percentage absorbed were made from data taken on hydrogen sulphide and dried air against atmospheric air and these were found to reproduce one another even in minute details. A similar curve was plotted of data taken on wet hydrogen sulphide against atmospheric air. The resulting curve appeared as a mirror image of the previous ones.

In Fig. 1 curve *A* represents ratios of transmission through the cell filled with dry hydrogen sulphide and through the cell filled with dried air. On another occasion a curve was made representing ratios of data taken on transmission through dry hydrogen sulphide and dry air. In spite of the fact that the data were all taken on the same day it was found that the humidity had changed a great deal during the time of the experiment. This curve was very similar to *A*. It indicated that the amount of water vapor displaced by the cell was less in the measurements made on dry air than those made on dry H_2S. This was actually the case since hygrometer readings showed showed the humidity at this time to be much higher than when the data on dry air were taken. Curve *B* is a sketch of Rollefson's curve for H_2S at 8.0μ placed there for comparison, while *C* represents the general appearance of Hettner's curve for water vapor in this region. We wish to call attention to the general agreement between that observed by us and Rollefson's curve and in addition to point out that nearly every maximum in Hettner's curve coincides with a minimum in our curve and vice versa.

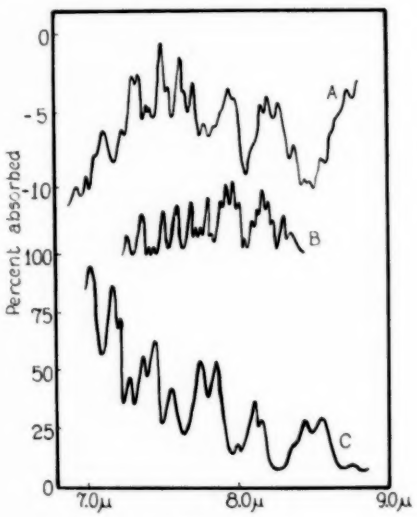

Fig. 1.

We suggest therefore, as an explanation of the band reported by Rollefson and by Mischke at 8.0μ in hydrogen sulphide, that it is not due to hydrogen sulphide, but rather due to water vapor falsifications which may arise when a long cell is used. This evidence is further supported by the fact that the spacings between the lines as given by Rollefson are of the same magnitude as those given by Sleator and Phelps[4] in their work on water vapor absorption rather than those observed in the bands of hydrogen sulphide.

H. H. NIELSEN
A. D. SPRAGUE

Ohio State University,
Mendenhall Laboratory of Physics,
April 6, 1931.

[4] W. W. Sleator, and E. R. Phelps, Astrophys. J. **62,** 28 (1925).

Measurement of the Kerr Effect in the Infrared Spectrum

The work of Szivessy and Dierkesmann (Ann. d. Physik (5) **3,** 507 (1929)) in extending dispersion measurements of the Kerr electro-optic effect beyond the customary visible spectrum into the ultraviolet would seem to call for a similar extension into the infrared, if

possible. This I have recently succeeded in doing, in the case of carbon disulphide, with an accuracy apparently not far short of that attained in visual measurements.

The apparatus consists of a spectro-bolometer with very sensitive galvanometer, operated in connection with a Kerr cell. This has plates 5×37 cm and 1.3 cm apart. Light from a special tungsten strip filament lamp is concentrated in a narrow conical beam to an image in the center of the cell, from which it diverges to be focussed later on the slit of the spectrometer. A large aperture double-image prism (only one of the images is utilized) polarizes the entering light in the 45° azimuth and a similar prism crossed at 90° serves as "analyzer." The electrostatic stress converts the plane polarized light into elliptical and the minor axis of the ellipse is proportional to the square root of the resultant galvanometer deflection. The phase difference is readily computed upon comparing the deflection with that produced by a known rotation of the polarizing prism. A high speed Wehrsen "Mercedes" static machine has so far served as a very satisfactory source of high potential.

The spectral range which can be explored in this way seems to be from about 0.5μ to 2μ or beyond, thus extending the previous wavelength range for this work some four-fold. Carbon disulphide, over this range, shows a dispersion of the Kerr double refraction in better agreement with the Havelock formula $B=C(n^2-1)^2/\lambda n$ than might reasonably be expected. There are some discrepancies, however, to be investigated more carefully later—and explained if possible. The method is to be further developed and extended to such other materials as have sufficient infrared transparency.

L. R. INGERSOLL

Physical Laboratory,
University of Wisconsin,
April 7, 1931.

Quantum Mechanics and the Chemical Bond

Three years ago I announced in a short note[1] the discovery of some new results regarding the chemical bond. It was pointed out that under certain conditions the formation of chemical bonds by an atom can destroy the distinction between s and p eigenfunctions, and a criterion determining whether this change in quantization of the single-electron eigenfunctions will or will not take place was given. It was also announced that this change in quantization permits the formation of four equivalent tetrahedral bonds by carbon.

Since then a number of further results bearing on the nature of the chemical bond have been obtained; it is the purpose of this letter to call the attention of physicists to a paper in the April, 1931, issue of the Journal of the American Chemical Society in which they are given in detail. It was first shown from the quantum mechanics that the main resonance integrals for an electron-pair bond between two atoms involve only one single-electron eigenfunction on each atom. In consequence many properties of electron-pair bonds can be derived from a consideration of single-electron eigenfunctions alone. Thus it is shown that if $s-p$ quantization is not changed, the bonds formed by the p eigenfunctions will tend to be at right angles to one another. A very simple but powerful approximate *quantitative* treatment of bond strengths is given. With its aid it is shown that when $s-p$ quantization is broken through bond formation, the best bond eigenfunctions which can be formed from a combination of s and p eigenfunctions alone are tetrahedral eigenfunctions, so that the two, three, or four bonds formed will tend to make angles of 109°28′ with one another. This explains the tetrahedral angles found experimentally not only for quadricovalent carbon, nitrogen, silicon, etc., but also for tricovalent nitrogen, oxygen, etc. The tetrahedral eigenfunctions also allow free rotation about single bonds, but not about double bonds.

When d eigenfunctions as well as s and p are available for bond-eigenfunction formation a number of bond configurations are possible. One d eigenfunction with s and p permits the construction of only four strong bonds, *and these are directed towards the corners of a square.* Such a configuration has been shown to exist for bivalent palladium and platinum, and this theory predicts it also for bivalent nickel in $K_2Ni(CN)_4$ and for trivalent gold. Two d eigenfunctions give six strong bonds directed towards the corners of an octahedron; this configuration is found in many complexes.

[1] Linus Pauling, Proc. Nat. Acad. Sci. **14**, 359 (1928).

It is also shown that in complex ions the orbital magnetic moments of electrons are extinguished through the interaction with surrounding atoms, so that the magnetic moment is due to the spin moments of unpaired electrons alone. Together with the results obtained regarding bond eigenfunctions, this leads to a complete theory of the magnetic moments of polyatomic molecules and complex ions. With its aid magnetic data have been shown to provide verification of many predictions regarding bond eigenfunctions; and in a number of doubtful cases magnetic data provide a basis for definite decision as to the type of bonds in a given complex.

These results have also permitted the formulation of a set of principles determining the structure of crystals containing electron-pair bonds, to be published in the Zeitschrift für Kristallographie.

Three of these results have been independently obtained by Slater and announced in a preliminary communication.[2] He points out the possibility of the formation of four equivalent tetrahedral bonds by a carbon atom (as I did in 1928), without giving the tetrahedral eigenfunctions and without recognizing that tetrahedral eigenfunctions are also important even when fewer than four bonds are formed; and mentions that this leads to restricted rotation about a double bond. Having apparently assumed the importance of one single-electron eigenfunction to bond formation, he also shows that p eigenfunctions should lead to 90° bond angles.

LINUS PAULING

Gates Chemical Laboratory,
California Institute of Technology,
April 7, 1931.

[2] J. C. Slater, Phys. Rev. **37,** 481 (1931).

Time Lag in Changes of Electrical Properties of Rubber with Temperature and Pressure

An abstract of a paper by the author entitled "Time Lag in Changes of Electrical Properties of Rubber with Temperature and Pressure" appeared in the Physical Review, Vol. 35, page 1429, June 1, 1930. Data were presented which apparently showed that two or more hours might be required for the dielectric constant, power factor, and resistivity to become constant after the temperature had been changed. In attempting to check these results, an error in experimental technique was discovered. Measurements with improved apparatus show that the dielectric constants and power factor follow the temperature changes with little if any time lag. No additional measurements on rubber under pressure have as yet been made.

ARNOLD H. SCOTT

Bureau of Standards,
Washington, D.C.,
April 6, 1931.

The Uncertainty Principle

Kennard has connected the uncertainty principle with radioactive disintegration by showing (Phys. Zeits. **30,** 495–497) how to derive Gamow's formula for radioactive disintegration from known quantum principles plus the uncertainty principle of Heisenberg without the additional postulate assumed by Gamow that a particle of energy W can pass through a potential wall of height $V > W$.

Here we have the pure chance phenomena of radioactive disintegration, independent of the disturbance produced by the act of measurement, and performed for us by nature at a rate that has remained constant since the solidification of the earth's crust, linked with the probability phenomena of the new quantum mechanics, the indeterminateness of which is assumed to be caused by an uncontrollable perturbation introduced of necessity in the process of measurement.

Is it not better to leave the indeterminateness in nature where we find it, rather than to attribute it to the inevitable perturbation introduced when making an observation, although we do not know how this perturbation introduces the indeterminacy?

If we can believe that the general laws of quantum mechanics are fundamental laws of nature, the various possibilities of natural behavior should be inherent in these laws, whether they be of a physical, chemical or biological character. I shall not expatiate here on the considerable progress that has already been made by the application of the quantum laws to chemistry, by the work of Heitler, London, and Slater. The generality

of these laws, which is responsible for their abstractness, and their flexibility, as evinced in a concrete manner by the uncertainty principle, make for their adaptability to other domains of thought. One might expect that this generality and plasticity would be characteristic of fundamental laws of nature. Viewed in this light one need not make apologies for nature by attributing the indeterminateness in its laws to the limitation of our knowledge imposed on us by the very act of observation.* Although if one feels that somehow our fallibility does play a part in our picture of the universe, one might view the objective laws of quantum mechanics as bringing before us the subjective aspect of definition and concept. As for the uncertainty principle, one can, following Darwin (Proc. Royal Soc. **A130,** 1931), regard it in the same role as the part played by the clocks and rods in the early formulation of the relativity theory when it was necessary to supplement the formal theory by concrete examples showing how the old classical ideas failed in specific cases. The general laws of the quantum mechanics, which are at the bottom of the uncertainty principle, are not conditioned by a theoretical clumsiness in our means of observation.

The intimate connection between the indeterminateness in quantum mechanics and the concept of observation may be due to the fact that "observation" implies structure. We could not plan our experiments but with the supposition that the elementary entities of nature have a structure. But the elementary entities of nature have neither a particle nor a wave basis. It is only after quantization—after observation—that one can legitimately introduce space and time. The Schroedinger equation may be looked upon as controlling, in a statistical way, the space-time manifestations of the elementary entities of nature, although the equation itself is devoid of any geometrical interpretation. We make manifest the indeterminateness in nature by bringing over space-time concepts and space-time description to atomic theories that, in order to predict, must go beyond observation. If a scientific theory were humbled to be valid only as far as observation goes, what would happen to cosmogony and geophysics? Should one doubt the validity of scientific inference because it yields results that can not be expressed in terms of familiar things, that are beyond the range of our sensations? There are good reasons for believing that quantum laws are not laws which man's mind has imposed on nature but are laws which nature is having a rather difficult time imposing on man's mind.

Finally, if one does not try to elevate his preconceived ideas and intuitions about causality to a law of nature, but merely views causality as the assumption that nature can be comprehended, can be grasped in thought—though not in imagery—there is no failure of causality in quantum mechanics.

ALEXANDER W. STERN

Brooklyn, N. Y.,
April 11, 1931.

* Prof. J. E. Turner (Nature **126,** pp. 995) views the indeterminism in quantum mechanics as having nothing to do with causation but interprets "not determined" to mean "not ascertained." Other physicists argue that the uncertainty principle does not exclude exact laws from physics but means merely that we have no way of verifying them.

On the Effect of Resonance in the Exchange of Excitation Energy

It is well known that exchange of excitation energy between atoms on collision takes place most readily if the "resonance" between the two atoms is good, i.e. if the quantum states of the two atoms are such that the excitation energy of one nearly matches the excitation energy of the other, so that only a small change in the relative kinetic energy of the two atoms is necessary in order to effect the energy balance before and after the collision.

This point has been discussed by Kallmann and London (Zeits. f. physik. Chem. **2B,** 207 1929)) who came to the conclusion that the cross-section would in general be larger the better the resonance. Their calculation is very interesting but not entirely free from objections. It may, therefore, not be out of place to look at the matter from another point of view, perhaps itself open to some objections, but which I believe brings out the nature of the problem very clearly.

The Franck-Condon principle, which says that those transitions are most probable which disturb the motion of the nuclei the least, has been very successful in accounting for the intensities in band spectra, and it has also

been applied recently to the case of predissociation (Franck and Sponer, Göttingen Nach., 1928, 241; Herzberg, Zeits. f. Physik **61,** 604 (1930); Turner, Bull. Am. Phys. Soc. **6,** 16 (1931)). Now in the case under consideration we can treat the pair of atoms which exchange energy as an unstable molecule, draw potential energy curves for the electronic states of the "molecule," (similar to London, Zeits. f. physik. Chem. **11B,** 222 (1930)) and handle the transitions from one continuum to another in the same way that we treat, in the predissociation case, transitions which take place from a discrete state to a continuum. It may be well to point out, parenthetically, that the case of predissociation and the present case are really quite different from the case of adsorption or emission of radiation, and, naturally, the real justification of this use of the Franck-Condon rule will come when the matter has been given a more or less rigorous quantum mechanical investigation.

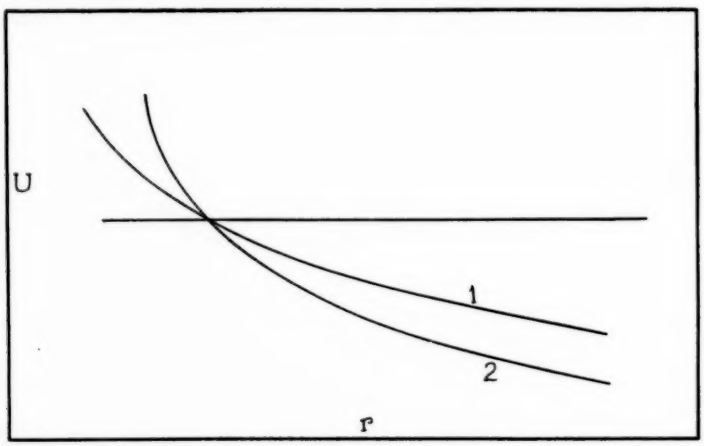

Fig. 1.

In Fig. 1 let curve 1 be the potential energy curve (potential energy $= U$, distance between atoms $= r$) with atom A excited, atom B unexcited, and let curve 2 be the curve with atom B excited, A unexcited. Suppose curve 1 represents the initial state of the pair of atoms. Then its intersection with a horizontal line gives the distance of closest approach of the atoms if they make a head-on collision with the energy indicated by the horizontal line. If curve 1, curve 2, and the horizontal line intersect at the same point, as shown, or somewhat near the same point, then, according to the Frank-Condon theory, we may expect a relatively large probability of transition provided, of course, the interaction between the atoms at this distance, r, is great enough. If the two atoms do not collide head on, this means that they have a relative angular momentum, and we can represent the situation by adding a term $(h^2/8\pi^2 M)\, j(j+1)/r^2$ to the potential energy, where M is the reduced mass, and j the rotational quantum number; but as a more or less rigorous selection rule for j will hold, practically the same amount must be added to the curve for the final state: they will therefore continue to intersect at the same value of r. Thus all collisions with this distance of approach will be favored. Collisions with something near this distance of approach will be somewhat less favored, and there will be a spherical shell in which favorable collision take place. Now it is seen that the closer together the asymptotic values of U_1, and U_2, in general the greater the distance r at which they will intersect, and hence, we may infer, the greater the size of the spherical shell in which collisions are favored by the particular factor under consideration. It may not be the only factor, and it certainly cannot stretch the region of favorable collisions out indefinitely, but all the indications from analogous cases are that it should be an important factor. The case where the asymptotic values of U_1 and U_2 coincide is just the case of exact resonance, and it is easy to see why transitions with exact resonance should be favored, but it is seen that the precise definition of good resonance is involved in complications which must be treated specially in any given case.

Of course, we cannot draw definite conclusions from such qualitative observations, but they at least provide a guide for future quantitative calculations. For the most part the applications of the Franck-Condon principle are just as qualitative as this one, but in the case of band spectra they have provided the stimulus for some successful quantitative work.

I have recently extended the quantitative work described in a preliminary note (Proc. Nat. Acad. Sci. **17,** 34 (1931)), where the force which acts between the two atoms is supposed to be due to their momentary dipole moments, by treating the two atoms as a molecule and using perturbations of the type introduced by Slater, (Proc. Nat. Acad. Sci. **13,** 423 (1927)). It appears, though with some assumptions I am trying to remove, that practically no transitions will take place unless the resonance is extremely good; the potential energy curves in this case do not intersect. Yet, experimentally, cross-sections very much larger than normal, or cross-sections unusually large for the type of transition considered, occur for such great resonance differences as 40 to 60 millivolts. I am inclined to think that other forces than the interaction forces of dipoles come into play, even when the radius of action is very large. Kallmann and London, themselves, noted that large cross sections would be expected when electron orbits are large.

It may be well to mention here that Eq. (5) of my preliminary article mentioned above, is incorrect. This error, which was carried through, should not make much difference in the final results and will be corrected later.

O. K. RICE

Chemical Laboratory,
Harvard University,
April 11, 1931.

The Formation of Striae in a Kundt's Tube

For the past seven years the author has been experimenting on striae formed in a Kundt's tube to determine, if possible, the cause of such striae. An article concerning the use of pith dust in a Kundt's tube was published by the author in Nature **118,** 157 (1926). In July 1929 he was able to show conclusively that a rotation of the dust particles on each side of a striation takes place; Phys. Rev. **36,** 1098 (1930); Science **72,** 442 (1930). January 14, 1931 the author made motion pictures of these rotations which take place on each side of each single striation. Fig. 1 shows an enlarged photograph of one such striation made from the motion picture negative. The black particles composing the striae were cork-charcoal. The striae were produced in a glass tube in which the air was compressed and rarefied by means of a metal piston attached to one prong of an electrically-driven tuning fork. Fig. 2 is a diagram showing the direction of the rotations taking place on each side of a single striation. Further details are given in the references above cited.

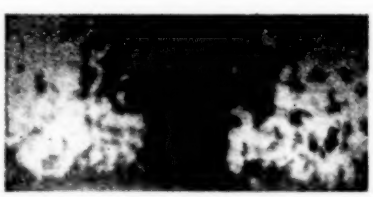

Fig. 1.

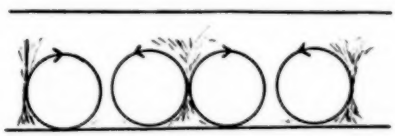

Fig. 2.

The striae in a Kundt's tube are formed by air vortices in the same manner as ripple-marks in sand are formed by water vortices. As shown by Darwin, Proc. Royal Soc. **36,** 18 (1883), these rotations are produced when an alternating fluid flow takes place about obstacles in its path. The clockwise and counter-clockwise rotations are maintained always in the same direction regardless of the fact that the fluid stream is alternating.

Also the author has shown that, when using cork particles of the same size, as the frequency of vibration of the air column in the tube increases, the average distance between striae becomes smaller. The photographs of Fig. 3 illustrate this fact. Also the author has shown that, with a constant frequency of vibration of the air in the tube, as the cork particle size is made smaller, the distance between adjacent striae becomes less. The photographs in Fig. 4 illustrate this fact.

The above mentioned observations will be discussed more in detail in a forthcoming publication. In this publication the author will discuss also the formation of striae which he succeeded in producing on a glass rod wet with alcohol, during the summer of 1925; the absence of striae in a vacuum; the production of striae by an interrupted air stream when the frequency of interruption was too low to produce an audible tone; and some photographs which have been made showing that the strain in a stroked glass rod clamped at its middle point increases in a direction from a point at the free end to a point at its center. The experimental work demonstrating all the above mentioned facts has been done by the author.

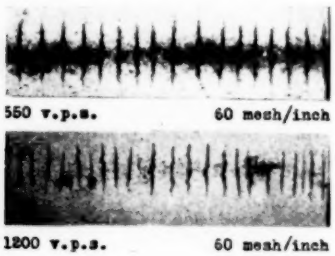

Fig. 3.

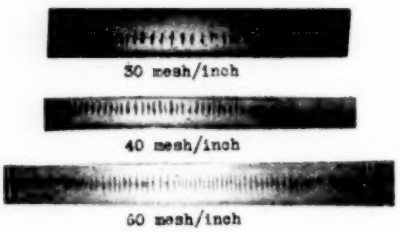

Fig. 4.

ROLLA V. COOK
Bethany College and
Indiana University, U.S.A.,
April 15, 1931.

Zodiacal Light and Magnetic Disturbance

During a recent trip southward along the 75th meridian from Norfolk, Virginia, to Cape Maisi, Cuba, we observed the zodiacal light. In the evening of March 13, 1931, when the observations were begun, the zodiacal light was unusually bright, the zodiacal cone at 8 P.M. could be followed up to and beyond the Pleiades which were about 40° from the horizon. The zodiacal light was again strong during the evening of March 14. The following evening, March 15, the zodiacal light was distinctly weaker than on the preceding two evenings and for the next three evenings to March 18 it remained fairly weak, that is, it was of its normal brightness. We tried to make morning observations but had no success because Venus, which was in the morning sky, was bright enough to obscure the morning zodiacal light.

After our return from the voyage we found that the magnetic activity was zero from March 1 to 10, a moderate disturbance began March 11 or 12 and died away on March 14, with magnetic calm from March 15 to 20. The magnetic data were obtained from the observatories at Cheltenham, Maryland, Tucson, Arizona, and Meudon, France, the data from Cheltenham being kindly furnished by the U. S. Coast and Geodetic Survey, and the data from Tucson and Meudon being taken from the Cosmic Data Broadcasts of Science Service. It is seen that the zodiacal light was unusually bright during the period of magnetic disturbance. This is in keeping with the atmospheric ion theory of the zodiacal light and the gegenschein (Phys. Rev. **35,** 1098 (1930)).

C. BITTINGER
E. O. HULBURT
Naval Research Laboratory,
Washington, D. C.,
April 17, 1931.

BOOK REVIEWS

Handbuch der Spectroscopie, von H. KAYSER UND H. KONEN. Siebenter Band, Zweite Lieferung. Pp. 499–750. S. Herzel, Leipsig, 1930. Price RM28.

The second part of Volume 7 of the Handbuch der Spectroscopie is an eloquent testimonial to the industry of the authors. As they point out, such a compendium can only be a continuous affair, to be added to from time to time as observations on spectra multiply and their interpretations develop and crystallize into more comprehensive form. Even should our summaries of data and systems of notation become more condensed than at present, the "Handbuch" will never cease to be a mine of information for the laboratory spectroscopist.

This latest addition to the "Handbuch" contains bibliographies and tables of wave-lengths for gallium, gadolinium, germanium, hydrogen, helium, hafnium, mercury, holmium, indium, and iridium. For each element there is also a condensed summary of the literature. In cases where the classification of the lines into series has been made, the term designations of lines are included; modified notation following those of Fowler and Paschen being used for all simple cases, and the notation of the original authors being used where the spectral structure is complicated. The simple notation used is the same as in the first part of Volume 7, i.e., large Latin letters for singlets, large German letters for doublets, and small Latin letters for triplets.

For each element the bibliography is also completed to include all articles written since the issue of Volume 5 to the year 1927. Although none published later than 1927 are included, the number of references is enormous, reflecting the immense amount of spectroscopic research done during the years since the fifth and sixth volumes of the "Handbuch" were issued. For instance, in Volume 5 of Kayser's "Handbuch" there were 177 references to papers on hydrogen spectra, while the present volume contains 549. In spite of the fact that the spectral notation employed is not in accordance with modern usage, the collection of references in a few pages makes this latest addition to the "Handbuch" invaluable. There are very few misspellings and misprints. The print is clear, on good paper, and in the style so well known to those who have had occasion to use the "Handbuch." One looks forward to the volumes yet to appear, containing references and data for the remainder of the elements.

GEORGE MONK

Elektrophysik der Isolierstoffe. DR. ANDREAS GEMANT, Pp. 222+vi, figs. 76. Verlag von Julius Springer, Berlin, 1930. Price bound RM 21.50.

The causes of loss and absorption of energy in dielectrics are only very incompletely understood at the present time. But in recent years there has been a renewed interest in these problems and considerable progress has been made with them. It is therefore fitting that the present volume should appear. It is written by an able worker in this field and deals with both the scientific and engineering aspects of the subject. The book is evenly divided into two sections one in which the normal behavior of insulating materials is discussed, and the other in which breakdown phenomena are considered.

Under normal operating conditions losses in dielectrics result from the presence of either or both ions and dipole molecules. The theories which describe the various mechanisms are clearly and exactly given. On controversial points, of which there are many, the different view points are usually presented, after which the author gives his position and states why. A feature of this section is the discussion of the theories of P. Debye and of K. W. Wagner which, although they result from descriptions of entirely different mechanisms, are shown to lead to mathematical expressions of the same form for the power factor and dielectric constants as functions of temperature and frequency, indicating that only by means of the most exact measurements will a differentiation between them be possible.

The second section treats breakdown phenomena in gas, liquid and solid dielectrics, with particular reference to the work of Joffé, Peek, Rogoski, Slepian, Townsend and Wagner. As in the first section the experimental methods of measuring the various quantities involved are

but briefly given, if at all, while theoretical discussions are in some cases quite complete. Concluding paragraphs are devoted to general statements concerning the influence of the physical and chemical nature of a material on its dielectric strength. The physical characteristics are believed to be the much more important.

The book might perhaps have been improved in several respects.

1. Page 76. Since the effect of extremely high frequencies on the conductance of a very dilute ionic solution is mentioned it should have been treated more exactly. It leads to an increased conduction because the ionic atmosphere which is formed about the ion can not in this case become dissymetrical, and not because the atmosphere can not form at all as in the case of the Wien effect.

2. Pages 85–90. The work of Phipps and his students on the conductivity of crystals is at least deserving of mention. The theory of Smekal which postulates an ionic conduction in lattice imperfections might also have been mentioned at this point since it apparently has found favor with many investigators.

3. In certain cases purely chemical facts concerning a particular insulating material have enabled the assignment of a mechanism to the conduction process taking place in it. Therefore there could have been included suggestions concerning the actual chemical composition of some of these materials. The colloid chemistry of insulating materials is also important.

4. The author list with journal citations might well have included page references to the text.

These suggestions are not intended to indicate an adverse judgement of the book. The arrangement content and manner of presentation are admirable. It can be recommended not only as a book which will make it easy to become acquainted with this important subject but also as one which will stimulate the interest of a research worker in this field.

J. W. WILLIAMS